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# CRUDE RUBBER

AND

## COMPOUNDING INGREDIENTS

### A TEXT-BOOK OF RUBBER MANUFACTURE

By HENRY C. PEARSON, F.R.G.S.

Editor of *The India Rubber World*

Author of "What I Saw in the Tropics," "Rubber Tires,"

"The Rubber Country of the Amazon,"

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TO  
**Professor William C. Goldsmith**  
FOR MANY YEARS  
PRINCIPAL OF THE PUNCHARD FREE SCHOOL  
ANDOVER, MASS.  
WHO FIRST AWAKENED THE AUTHOR'S INTER-  
EST IN BOTANY AND CHEMISTRY  
THIS VOLUME IS AFFECTIONATELY DEDICATED

## PREFACE.

SINCE the first edition of this book appeared, almost twenty years ago, the rubber business has grown notably. New sources of rubber have been developed in various parts of the world, and grades of rubber heretofore unknown have come into use. Plantation rubber, previously a negligible factor, has taken its place as a regular and dominating product. Progress in the reclaiming of waste rubber of all sorts has been constant and of great magnitude. The industry at large preserves the same general outline as formerly, with perhaps the single exception of the making of motor tires, today the greatest division in rubber manufacture. Of new compounding ingredients there are many, of substitutes a great variety, and of processes, good and bad, thousands. In the revision of the book those of a real or a suggestive value have been utilized. The general plan of the book has not been altered. It remains a dictionary of compounding facts, an encyclopedia of rubber-factory practice. It is for rubber-factory use and bespeaks for itself the same favor that it found with the practical man when it first appeared.

The superiority of such a collection over the most comprehensive book of compounds doubtless will be apparent to the expert manufacturer, for this reason: When a manufacturer buys a set of compounds—and most of them are purchasable—he invariably acquires them not so much for use as for suggestion and comparison. The descriptions, therefore, of a great majority of the ingredients used in all lines of rubber compounding, and scores with which he may be unfamiliar, will be so suggestive to the practical man that new sets of compounds will be secured, each partaking of the individuality of the expert, and bearing the impress of the line of work done in the factory to which he is attached, and wholly free from the taint of imitation or counterfeiting, which is the bane of the purchased secret. It is felt that another point of superiority over the mere compound book will be found in the fact that no private formulas are given, those which are cited being typical rather than specific.

In the ten years that have elapsed since the second edition of this work appeared, great changes have taken place in rubber production and in processes of manufacture. The rise and dominance of cultivated rubber, the use of accelerators, the pressure cure, instead of the open dry heat, the progress in synthetic rubber production, are but a few of these.

In the compilation and revision of this book free use has been made of English, German, and French standard technical works, as well as of technical journals, such as *The India Rubber World*, *The India-Rubber and Gutta-Percha Trades Journal*, *Le Caoutchouc et la Gutta Percha*, the *Gummi-Zeitung*, *The Journal of the Society of Chemical Industry*, and others.

The author takes pleasure in acknowledging his indebtedness for helpful suggestions to skilled manufacturers and superintendents in both America and Europe, and to the following distinguished writers: P. G. W. Typke, F.C.S.; William Thompson, F.R.S.E.; H. Grimshaw, F.C.S.; W. Lascelles-Scott, F.R.M.S., M.S.C.I.; Richard Gerner, M.E.; Dr. C. Purcell Taylor; Thomas Bolas, F.C.S., F.I.C.; Professor D. E. Hughes, F.R.S.; Granville H. Sharpe, F.C.S.; Carl Otto Weber, Ph.D.; Lothar E. Weber, Ph.D.; A. Camille, the late Dr. Eugene F. A. Obach, F.I.C., F.C.S., M.E.E.E.; Philip Schidrowitz, Ph.D.; Dr. Joseph Torrey, Dr. David Spence, Professor Francis Ernest Lloyd, Hubert L. Terry, F.I.C.; Cuthbert Christy, F.R.G.S., and many others.

I have great pleasure also in gratefully acknowledging the assistance of members of my staff in the onerous work of proof-reading, indexing, etc. My thanks are also extended to Webster Norris, S.B., for his work in the revision of the technical and chemical portions of the volume.

# CONTENTS.

Preface .....	3
CHAPTER I.	
Crude Rubber, Chemical and Physical Characteristics. Sources of Supply. Grades: Para, Central, African, and East Indian Gums. Origin of Trade Names. Botanical Details. Plantation Rubber .....	7
CHAPTER II.	
Some Little Known Rubbers and Bastard or Pseudo-Gums; Possibility of Development of Their Use in the Factory.....	32
CHAPTER III.	
Coagulation, Native Methods; Chemical Systems, Mechanical Systems, Coagulating Machines, Smoking, Oxydases .....	44
CHAPTER IV.	
Vulcanizing Processes and Ingredients, Sulphur, Antimony Sulphides, and Other Materials Used. Vulcanizing Pressures and Temperatures. Plantation Hevea and the Optimum Cure.	54
CHAPTER V.	
Accelerators, Organic and Inorganic.....	80
CHAPTER VI.	
Fillers and Ingredients Used in Rubber Compounds; Sources, Properties, and Uses of the Various Materials; Unusual Ingredients	89
CHAPTER VII.	
Substitutes for India Rubber, Natural and Artificial.....	117
CHAPTER VIII.	
Substitutes for Hard Rubber and Gutta-Percha, Including Cellulose Products .....	141
CHAPTER IX.	
Resins, Balsams, Gums, Earth Waxes, and Gum-Like Substances Used in Rubber Compounding .....	153

## CHAPTER X.

Coloring Matters. Blacks, Blues, Greens, Reds, Browns, Whites, and Other Colors in Hard and Soft Rubber.....	176
---	-----

## CHAPTER XI.

Acids, Alkalies, and Their Derivatives Used in Rubber Manufacture	194
---	-----

## CHAPTER XII.

Vegetable, Mineral, and Animal Oils Used in Rubber Compounds and Solutions .....	213
---	-----

## CHAPTER XIII.

Solvents Used in Commercial and Proofing Cements; Their Origin, Properties, and Methods of Use.....	228
--	-----

## CHAPTER XIV.

Miscellaneous Processes and Compounds for Use in the Rubber Factory: Waterproofing Compounds; Shower-proofing; Deo- dorization; Preserving Rubber Goods. Shrinkage of Rubber. Tire Fillers and Puncture Fluids.....	247
--	-----

## CHAPTER XV.

Synthetic Rubber .....	269
------------------------	-----

## CHAPTER XVI.

Vulcanization Without Sulphur .....	275
-------------------------------------	-----

## CHAPTER XVII.

Reclaimed Rubber and Its Uses.....	290
------------------------------------	-----

## CHAPTER XVIII.

Physical Tests and Analysis of Crude and Vulcanized Rubber. Specifications for Rubber Goods. Specific Gravity.....	302
---	-----

## CHAPTER XIX.

Primary Processes, Divisions in Rubber Manufacture, and Typical Compounds .....	351
--	-----

## CHAPTER XX.

Gutta-Percha: Its Sources, Properties, Manipulation, and Uses; Components of Gutta-Percha; Vulcanization; Gutta-Percha in Compounds; Methods of Analysis.....	376
---	-----

Index .....	399
-------------	-----



## CHAPTER I.

### CRUDE RUBBER, CHEMICAL AND PHYSICAL CHARACTERISTICS, SOURCES OF SUPPLY, ET CETERA.

INDIA RUBBER is hard to define in scientific language. Its atomic structure is difficult to express, and means little when expressed. It is a hydrocarbon, with the approximate formula  $C_{10}H_{16}$ ; but some oxygen is always present, which has led some to believe that oxygen is a necessary constituent. As a rule, however, the presence of oxygen is considered injurious, or a sign of deterioration. Rubber is as readily attacked by oxygen as is iron, and as surely destroyed by it. The formula  $C_{10}H_{16}$  is of too general a nature to be of value, since it covers rubbers of widely different physical properties, and even includes gutta-percha. A more important chemical fact is that rubber is extremely resistant, being soluble only in carbon disulphide, carbon tetrachloride, turpentine, ether, gasoline and the like.

The physical properties of rubber are softness, toughness, elasticity, impermeability, adhesion and electrical resistance. Its most characteristic, but not most important property, is that it can be repeatedly stretched to many times its length, returning each time to about its first dimensions. No other substance is at all comparable to rubber in this particular property, though one or more of the other properties are possessed in turn by many other substances.

Rubber is derived chiefly from the milk or latex found in the bark of many trees, shrubs and vines, and to a certain extent also in the fruit, leaves, soft wood, or roots. The great families of the *Euphorbiaceæ*, in tropical America, and the *Apocynaceæ*, in tropical Africa, furnish most of the world's rubber. The *Artocarpaceæ*, of Central America and the East Indies, have a certain importance, and the *Compositæ*, *Asclepiadaceæ* and perhaps other vegetable families contribute a certain amount. Altogether there are some thousands of species of trees, vines, bushes, weeds, roots, and tubers which contain rubber; but the *Hevea*, of Brazil, the *Landolphia* and *Funtumia*, of Africa, and the

*Castilloa*, of Central America, together furnish practically the whole of the world's rubber. The tropics hold a vast store of wild rubber; but transportation, in these regions, is so difficult, and the growth of rubber trees under cultivation so rapid, that it is easier to grow rubber in accessible places than to get it out of the deeper forests; with the added advantage that plantation rubber is better prepared than would generally be possible in the forest.

The latex, from which rubber is derived, is most often white, but is sometimes red or yellow. It is usually thick, like cream, though the solid matter contained may vary from 20 to 60 per cent.

It has never been definitely settled whether the rubber exists as such in the latex, or whether it is developed by the process of coagulation. Some latex curdles immediately and spontaneously, like blood; others require the addition of chemicals or natural fermentation, like animal milk. In many cases the latex has never been made to coagulate. In some cases latex is used as a beverage, while in others it may be highly caustic or a deadly poison.

Another substance developed out of the latex, along with the rubber, is commonly called resin. Some regard this as a broken-down, oxidized, perverted or "unripe" rubber. Other authorities maintain the existence of a series of resin-bearing tubes in the bark, independent of the system of milk tubes, but drawn out with the rubber milk by the same bark cuts.

Rubber is composed of two substances or "principles," one of which, the adhesive principle, is easily soluble in ether, carbon disulphide, and the like; while the other, the nervy or structural principle, is never really dissolved. The adhesive principle corresponds roughly to starch, while the nervy principle corresponds to cellulose. The adhesive principle seems to vary directly with the resin content, without being quite identical with it. There seems to be nothing else in nature which even approximates the insoluble or nervy part of rubber. It is this which gives rubber its elasticity, and enables it to take up compound; hence it forms the basis of rubber valuation. The adhesive principle, quite useful in cements and

"frictions," forms the basis of a great number of "rubber-likes," and is of much less value.

In the succeeding pages the leading kinds of rubber are described and classified according to commercial usage, while reference is made also to the geographical distribution of rubber.

The Amazon valley, embracing hundreds of thousands of square miles of rubber-yielding forests in Brazil, Bolivia and Peru, is the center of the South American rubber industry, the whole product formerly being exported from the city of Para, whence the name "Para rubber." Several species of the *Hevea* produce this rubber, the best known being the *Hevea Brasiliensis*. Peru, Bolivia and Brazil also produce a rubber known as "caucho," and, in some markets, as "Peruvian rubber." This is the product of the *Castilloa Ulei*. Another species, *Castilloa elastica*, is the rubber tree of Nicaragua and other Central American states, which is also found in Ecuador, Venezuela, Colombia, and Mexico, and yields the rubber known as "Centrals." The Atlantic states of Brazil, south of Para, produce other rubber trees, from which come the grades known as "Mangabeira" and "Maniçoba."

"African" rubber is inferior to that obtained from South America, but through improved processes in gathering and curing, the various sorts are delivered in much better condition year by year. African rubber is found on both the east and west coasts and throughout the great basins of the Congo and Niger rivers, in the Soudan region, and also on the island of Madagascar. The *Landolphia*, which include the *Carpodinus* and the *Clitandras*, are vines or creepers from which is produced much African rubber. A considerable amount has been gained from such trees as the *Ficus Vogelii* and particularly the *Funtumia elastica*, which yields "Lagos" rubber.

The East Indies today furnish but little wild rubber. The first rubber exported from that part of the world came from the *Ficus elastica*, from Assam, the name of which province has attached itself to rubber from other regions as well. The islands of Java, Sumatra, and Borneo, also Penang and other states in the Malay peninsula, and likewise French Indo-China, produce a certain amount of rubber, mostly from vines or creepers.

Seaports, trading posts from which the first shipment is made, the name of a colony or country, or descriptive terms, as "thimbles," "buttons," "strips"—all or any of these may serve for names of different grades of crude rubber. A complete market report would indicate that there are a great number of different qualities of rubber, many coming from the same source. This, however, is not wholly true. Take, for instance, the Para grades: Years ago any rubber coming from Brazil was called Para rubber. Later it was divided into "fine," "medium," and "coarse." Then the rubber from the islands in the lower Amazon became known as "Islands rubber," while that coming from further up stream was known as "Upriver," and these, too, were divided into fine, medium, and coarse. Now a dozen or more local names are applied to rubber from different localities, tributary to the Para market. At the same time, most of these rubbers sell at the same figures, grade for grade, with the exception of coarse.

Something like this is true in the African rubber trade. For instance, a great number of local names are applied to the Congo rubber. The difference between "Equateur," "Kassai," and "Lopori" sorts may not be greater than between different lots from the same place. With a very few exceptions, the names which follow are those used commonly in the leading markets of the world:

#### PARA RUBBER.

RUBBER is classified at Para and Manaos into three grades, designated by the Portuguese words *fina*, *entrefina*, and *sernamby*. These grades in the United States are known as "fine," "medium," and "coarse," while in England they are classified as "fine," "entrefine," and "negroheads," the latter being divided to provide for a subgrade, "scrappy negroheads." The proportion of these grades exported through Para has been about 61 per cent. of fine, 11 per cent. of medium, and 28 per cent. of coarse.

FINE PARA rubber comes in large bottles or balls and, when cut, shows a surface closely marked with lines corresponding to the number of layers of rubber milk added during the smoking process. These layers are easily separated and,

when stretched, are very transparent. This rubber smells not unlike smoked bacon.

MEDIUM OR ENTREFINE resembles "fine," but is not so well cured, curds and globules of milk not perfectly coagulated being found between the layers.

COARSE OR SERNAMBY is made up of the residue, scraped from the collecting vessels, or from milk which has curdled before it could be smoked and made into "fine." This grade takes its name from the supposed resemblance of the scraps to the mussel fish called by the Portuguese *sernamby*. This rubber is known in England as "Negroheads" when in large chunks, more usual in the case of Upriver supplies.

Besides this general classification of Para rubber, other names are in use, derived from the localities of origin.

ISLANDS rubber is that produced on the island of Marajo, about 17,500 square miles in extent, and other islands in its vicinity in the delta of the Amazon, together with that from other parts of the state of Para, except the Xingu, Tocantins, and Tapajos rivers, which might well be called lower Amazon grades. The Islands "fine" and "medium" rubber is in the form of round or flat bottles, while the "coarse" or "sernamby" is in scraps massed into balls and round cakes, which give the name "negroheads" to this grade in the English market.

CAVIANA rubber, named from the island that produces it, is the highest grade of Islands, and is today marketed as a distinct sort. It has a smooth, close grain, and is much in demand for fine work.

CAMETA rubber is so called from the port of that name, on the Tocantins river. It is noted for the superior quality of its "sernamby" grade, the "fine" being the same as from the islands, but rarely seen. This rubber comes in the form of little cups pressed into large "negroheads."

ITAITUBA rubber comes from the port of that name, at the head of steam navigation on the Tapajos river, which enters the Amazon at Santarem. Rubber from this river is distinguished for the rather gutty quality of the "fine" and "medium," and its stringy, dirty "sernamby."

XINGU rubber, from the Xingu river, is noted for the specially good cure of the "fine."



UPRIVER rubber includes the product of the country bordering the Amazon and its tributaries above Para, and that which comes from Peru and Bolivia through the large streams rising in those countries—such rivers are the Purus, Jurua, Javary, and Madeira. This rubber comes to market in biscuits and balls varying greatly in size and shape, a full average biscuit weighing about thirty pounds. The difference in price between Upriver and Islands rubber is due chiefly to the fact that the former, being derived from more remote localities, shrinks less after arriving in market. Upriver rubber is marketed also under such local names as “Manaos,” “Madeira,” “Bolivian,” “Purus,” etc.

MANAOS rubber is named and exported from the city which is the capital of Amazonas, 1,200 miles up the Amazon river and the center of the rubber trade of the district.

MADEIRA rubber, named from a great river which joins the Amazon below Manaos, is of excellent quality and produced in large quantities. It has a finer and closer grain than any other Upriver rubber except the Bolivian.

PURUS rubber comes down the river Purus, the largest of the rubber-yielding tributaries of the Amazon, and is probably the choicest of all the Para grades. A certain amount of the output of the Purus comes from a region formerly belonging to Bolivia, from which it was marketed as “Bolivian” rubber. That region has been acquired by Brazil and organized into the Federal territory of the Acre, which continues to produce a large amount of rubber.

BOLIVIAN rubber is floated down the Beni and other rivers in Bolivia to the Madeira, and thence to the Amazon. It formerly met innumerable detentions from the cataracts in the upper Madeira, on account of which it became somewhat dried before reaching market. It has the advantage of being cured by a better class of labor than is common in Brazil, of having a tougher fiber and of being cleaner than most Upriver rubber, for which reasons it brings higher prices than any other.

Not all the rubber of the Para grades now comes down the Amazon. A certain amount of the Bolivian output is shipped overland to the Pacific, and some by river to southern Atlantic ports.

PERUVIAN rubber, in "ball" and "slab," was formerly applied, in the English trade particularly, to the class of rubber which will be described under the heading "caucho." In recent years however, Peru has supplied considerable rubber of the same character as Para—being derived from the *Hevea*. This rubber is exported from Iquitos down the Amazon, most of it going to Europe, where it is sold as Peruvian fine and negroheads (coarse), as well as ball and slab, and also "Peruvian weak." To a large extent Peruvian fine rubber loses its identity between Iquitos and the consuming markets, and is classed merely as Para.

MOLLENDON rubber comes from southern Bolivia, being transported by steamers across Lake Titicaca and by rail to Mollendo, a Peruvian port on the Pacific, and thence principally to England. It is prepared in biscuits and sheets and is marketed at a price between Upriver and Islands.

ANGOSTURA rubber comes down the Orinoco in Venezuela, from Ciudad Bolivar, which town formerly was known as Angostura. It is of the same grades as the Para sorts. Some of the same class of rubber finds its way into Brazil, at Manaos, where its identity is lost.

ORINOCO rubber is the same as "Angostura."

MATTO GROSSO rubber is from the state of that name in the southwest of Brazil, and reaches the market partly through tributaries of the Amazon and partly through the Paraná, which discharges into the river La Plata. It comes in "fine," "medium," and "coarse," but principally the latter, little of it reaching the market at present.

CAUCHO, which figures in all the markets of the Amazon region, and in statistics of Para rubber generally, is a distinct sort of rubber, inferior to Para, collected from the *Castilloa Ulei*. It is not cured by smoking but by admixture with the milk of lime, potash or soap. The physical characteristics of caucho, in the main, are the same as the Central American rubbers. The rubber of this sort exported by way of the Amazon formerly was obtained principally from Peru, but it has now been discovered throughout most of the rubber-producing regions of Brazil and Bolivia as well. Caucho figures very largely in the

Para rubber trade. It comes to the market in three forms—"ball," "strip," and "sheet" (or slabs)—ranging in value in the order named.

*Caucho* is the Spanish word for india rubber in general. When this particular sort of rubber first began to be marketed, it was obtained only in Spanish-speaking regions, and on coming down to Para, where the commercial language is Portuguese, and being rubber of a distinct type, it not unnaturally became known commercially by the Spanish name, which really was a most convenient form of describing it, so as to avoid confusion in the trade. The commercial designation of rubber in Portuguese, in use at Para, is *borracha*.

#### CENTRAL RUBBERS.

CENTRAL AMERICAN rubber, or "Centrals," includes that which is produced in all the states north of the Amazon valley, up to and including southern Mexico. It forms a distinctive class, being the product of a tree (the *Castilloa elastica*) not native elsewhere. In the United States the consumption of Centrals was once larger than that of Para rubber, but the yield has declined gradually to small proportions. This rubber is in good demand for certain uses, ranking in price below coarse Para. It has not the toughness or strength of fine Para, and possesses less elasticity. Centrals are classed usually as "sheet" and "scrap," besides which the terms "strip," "slab," "ball," and "sausage" are used. Greytown being a common shipping-point for Centrals, there is much confusion, one sort often getting substituted for another. Most of the yield of Costa Rica is exported through Nicaragua. The treatment of Centrals generally consists in mixing with the latex the juice of the "amole" vine, often in a hole in the ground, the product being "sheet" rubber. The rubber drippings which adhere to the bark of the tapped trees are peeled off when dry and called "scrap." The trade names below apply to the locality of origin, rather than distinctions in quality.

NICARAGUA rubber includes more than the product of that republic. The real Nicaragua rubber is drier, as a rule, than other grades of Centrals. Nicaragua sheet comes to market less



clean than formerly, and the scrap brings a better price. Greytown scrap is the best grade of Nicaragua rubber.

GUATEMALA rubber is inferior and unequal in quality. The best is whitish in color, and the lower grades black with a tarry appearance. In curing, the rubber-gatherers pour the milk upon mats to dry, afterwards pulling off the product in sheets, pressing them together for shipment.

GUAYAQUIL STRIP, from Ecuador, is imported in two grades—good and ordinary. Like the Guatemala rubber, the best has a whitish appearance. The inferior sort is porous and filled with a fetid black liquid, which carries an almost indelible stain.

ESMERALDA rubber, which also comes from Ecuador, is classed as “strip” and “sausage,” the two grades coming to market in about equal quantities.

COLOMBIAN is a pressed strip rubber, dark in color, sometimes showing white when cut. It is graded “No. 1” and “No. 2.” Some of the rubber from Colombia bears local designations, besides varying in quality. These include:

*Cartagena*, strip rubber, dark and tough, graded “No. 1” and “No. 2,” selling at less than “Colombian.” It comes also in thin sheets, rough or “chewed” in appearance, and tarry or sticky. The production has decreased very much of late.

*Virgin* or *Virgen* rubber comes from Colombia in “sheet,” “strip,” and “slab.” It is a product of a different tree (the *Sapium tolimense*) from the other “Centrals” described here.

PANAMA rubber, like that from Nicaragua, embraces a wide range of quality. The Pacific mail steamers bring together at Panama rubber from numerous ports, and confusion of grades is a result. What is marketed as “Panama” comes in “sheet” and “strip.”

MEXICAN rubber is of fair quality, but is received in constantly decreasing quantities. The grades, listed in the order of their selling value, are “ball” (or scrap), “strip,” and “slab.”

*Tuxpam strip* comes from the Mexican port of that name. Very little of it is received, and that not of uniform quality.

HONDURAS STRIP is of a quality similar to the Mexican, but is little produced.

WEST INDIAN rubber has a good reputation for quality. It is not produced on the islands, but comes from Venezuela and Central America, and the designation is simply a general trade name used in England.

It is to be kept in mind that the information given thus far under the general heading of "Central rubbers" relates to the native forest supplies from the countries mentioned. The product of the cultivated *Castilloas* is uniformly of a higher grade, is cleaner, and shows much less shrinkage.

The grades which follow, though not entitled geographically to be included as "Centrals," are in fact so classed, on account of their quality.

MANGABEIRA rubber, from the *Hancornia Speciosa*, is so called from the local name of the tree producing it, in some of the Atlantic states of Brazil, south of Para. It is an alum-cured rubber and comes in sheets of a tawny red color, which resemble slices of liver. The thin sheet sells for more than the thick, as it is drier and better cured. Occasionally it comes in the form of balls. It is exported from Pernambuco, Bahia, and other points on the coast.

PERNAMBUCO is another name for Mangabeira rubber, derived from the principal state and port from which it is shipped.

SANTOS rubber, from another port, is also Mangabeira.

CEARA.—Ceara rubber comes from a small tree particularly abundant in the Brazilian state of Ceara, known as the *Manihot Glaziovii* and the *Manihot dichotoma*. The milk exudes from the tree and coagulates in the form of "tears," which are gathered in scraps and balls. Of late years the rubber of the region referred to has received much attention and the output has been greatly increased. It has come to be known more generally by the local name of the tree, "Manicoba," of which there are now recognized to be several distinct species. One of these, the *dichotoma*, yields a superior quality of rubber, which is marketed as "Jequie" and "Remanso," these being locality names. It is also known as mule gum.

GUAYULE is a Mexican rubber of a relatively new type which has come into use to a very large extent. This rubber is obtained

from a shrub peculiar to the arid regions of northern Mexico and southern Texas—being practically the only rubber found in the United States. It differs from most rubber-producing plants in that it has no latex, the rubber being chiefly in the cells of the bark, a little in the wood, and none at all in the new shoots or leaves. The bark also contains balsam-like resins which are extracted with the rubber and are the cause of its softness and stickiness as compared with fine Para, for example. Generally the extraction of the rubber resolves itself into two processes: one purely mechanical and the other partly mechanical and partly chemical. Botanically the plant from which Guayule rubber is obtained is known as *Parthenium argentatum*. Guayule is also known as Pickeum gum.

#### AFRICAN RUBBERS.

AFRICAN rubbers, as a class, are more adhesive and less elastic than Para rubbers, ranking with or below Para negro-heads. They often contain a liberal percentage of impurities, and for a long time their disagreeable odor and intractable nature hindered their introduction. But advancing prices for Para grades and fear of their coming scarcity led manufacturers to experiment with African rubbers, until many uses were found for them. The result was a notable offset to the general upward tendency in price of the Para grades, although there are many purposes for which Africans never have been considered as competing with them. At the same time, the possibilities in the way of utilizing African sorts have not been exhausted, each year bringing out new uses. Besides, more intelligent supervision of the work of preparing rubber in Africa has led to a great improvement in some grades, as compared with the condition in which formerly they came to market.

The African rubbers are obtained from giant creepers, of which there is a score or more species on the continent and in the island of Madagascar, and also from several trees, the most important one of which, discovered first in the Gold Coast Colony, is known now to be widely distributed. There is now also a considerable production of "root rubber," obtained from underground creepers and marketed as "Lower Congo thimbles," and also as "Benguela," according to the sources of pro-

duction. The adulteration of African rubbers is not uncommon, being due to the dishonesty, not only of native gatherers, but doubtless also of some foreign traders on the coasts. But in most of the European colonies in Africa stringent regulations have been adopted to prevent such adulterations. On the Gold Coast the lumps of rubber brought to market by the natives were formerly cut into strips or buttons by machinery, before being exported. Latterly some of this work has been done in England, the rubber then being known as "Liverpool pressed."

As a rule, African rubbers are obtained by the destruction of the trees or vines with the result that the total receipts from that continent are decreasing, despite higher prices than prevailed formerly.

**BALL** is the classification of a large share of the African rubbers, which comes in every size from three or four inches in diameter down to half an inch or less. "Small ball" of the several kinds differs from the "large ball" in size, and is also dried and affords a smaller degree of shrinkage.

**THIMBLES.**—The natives, after gathering this rubber, cut it into cubes, about an inch square or less. Thimbles generally contain bark and sand, but very little moisture.

**NUTS.**—Rubber thimbles from Ambriz are quoted sometimes in European markets as "Ambriz nuts."

**LUMP** rubber comes in large pieces, varying in size and of irregular shapes. When packed in casks the pieces often become massed together in transit. It is from the best of the lump rubber that the most desirable buttons and strips are made.

**FLAKE** comes in lumps, livers, and soft irregular masses, and is valuable in the factory chiefly for frictions and for softening compounds.

**PASTE** is similar in quality but lower in grade than "flake." Accra flake and Niger paste are at the foot of the list, in respect to prices. The Niger is the cleaner material.

**STRIPS** are lump rubber that is sliced and pressed by machinery before it is offered to the trade.

BUTTONS is a name applied to rubber similarly treated as in making strips, except that it is cut into small pieces, whereas strips have been marketed in every length up to ten feet.

BISCUITS is another name for "buttons."

OYSTERS is another name for "buttons" or "biscuits."

TONGUES.—Some rubber formerly came to market in long, narrow, tongue-shaped pieces. The same grades are now more frequently seen in the shape of large balls.

NIGGERS are of various sorts and from different sources. These rubbers are ball-like in some cases, having the appearance of masses of stringy rubber pressed together between the hands and wound into compact masses.

TWIST rubber is not unlike "niggers" in quality, but shows less shrinkage and differs in preparation and appearance. The string or strip-like pieces are wrapped about each other in order to give a twisted look to the balls.

The list of rubber grades which follows is based upon a geographical arrangement, beginning with the upper west coast of Africa:

#### FRENCH WEST AFRICA.

This is an extensive region, extending from the Atlantic eastward to the precincts of the Nile, from which in recent years a great amount of rubber has come to French markets, the various grades being designated generally by local geographical names. The leading grades now marketed from this region are:

CONAKRY niggers.

SOUDAN niggers and twists.

BASSAM niggers and lumps.

LAHOU niggers.

GAMBIE "A," "A.M.," and "B." These last are of the "niggers" type.

#### GAMBIA (BRITISH).

GAMBIA niggers (No. 1, No. 2, No. 3)—These are classified according to cleanliness, No. 1 and No. 2 being fairly clean, and No. 3 containing considerable soil.

BATHURST.—Same as Gambia.



## SIERRA LEONE.

SIERRA LEONE TWISTS (No. 1, No. 2, and rejections).—This is white and amber in color, of low shrinkage, and has bark and grit in it, but little moisture.

NIGGERS (No. 1, No. 2, No. 3) are quite moist. No. 2 and No. 3 contain considerable soil.

CAKE.—Fairly clean; but wet. It is both red and white, the former bringing the better price.

MANOH TWISTS.—This comes in the shape of tightly wound cords of rubber and works soft. In color it is black or white, the black being the better.

## LIBERIA.

LIBERIAN.—This is graded as Lump, Hard Flake, and Soft. It cuts yellow, is very wet, and is often a soft pasty rubber.

## ASSINEE.

What is known as Assinee is graded as follows: *Assinee-Silky, Grand Bassam, Attoaboa, Lahou, Bayin, Half Jack*. It is like Old Calabar, only it comes in chunks three inches square, is wet, and cuts yellow. These names are chiefly used in the English market.

## GOLD COAST COLONY.

GOLD COAST.—This is chiefly lump from which Strips and Buttons are made. There are also Biscuits and Niggers (hard and soft). The Flake is wet and has a bad smell, but otherwise is quite clean.

ACCRA.—The Accra lump furnishes Strips and Buttons and is graded "prime," "seconds," and "thirds." The lower grades are Flake and Paste.

CAPE COAST.—This is another lump from which Strips and Buttons are manufactured and has for lower grades Flake and Soft.

SALT POND.—This Lump is also used in Strips and Buttons, the lowest grade being Flake.

ADDAH NIGGERS (graded as No. 1 and No. 2) is very similar to Sierra Leone, but generally in smaller balls. It is not an Accra rubber, nor are *Quittah Niggers* or *Axim*. As a

matter of fact, the grades from these different ports vary little if any, and are sold most frequently under the head of "Accra" rubber, from the name of the principal town in the colony.

TOGOLAND:

LOMI (or LOME) BALL.—The best grade of this is a clean, firm rubber and is fairly dry. The lower grades are rarely seen.

NIGERIA (INCLUDING LAGOS).

LAGOS.—This lump is also turned into Buttons and Strips, while soft inferior lumps are sold as low grades without manufacturing. It is very easily distinguishable from Accra by its odor.

NIGER.—The chief grade is Paste, which has an acid smell and is a low grade pasty rubber, wet but clean.

OLD CALABAR.—It is graded as Blue, Lump, and Niggers, and is very bad smelling. The best lump is undoubtedly used for strips and buttons.

BENIN BALL.—Is generally dirty and has a rotten, woody smell.

CAMEROONS.

CAMEROONS.—The ball is graded as large, mixed, and small; the clusters, which contain some fifty balls, as No. 1 and No. 2; and the knuckly ball, which is a small dry ball. This rubber has a fairly strong smell.

BATANGA BALL ("B," "E").—Same as Cameroons, Batanga being the name of a river and country in the Cameroons.

FRENCH CONGO.

FRENCH CONGO RUBBER is very similar to Cameroons, but the balls are larger.

GABOON is the best known flake and has for additional grades: lump, large "O" ball, and small "O" ball. The flake is free from dirt and is soft.

MAYUMBA is both ball and flake. Another grade known as Mixed is a combination of the two and is sold as second quality.

LOANGO.—Ball.

These are names of rubber stations on the coast. The natives boil rubber milk, adding the juices of vines, and, while

the rubber is hardening, wind it into balls, weighing from one-fifth pound to three pounds. The best rubber is not boiled, the milk drying on the wrists of the natives, as they tap the rubber vines. At the coast the balls are cut, to detect any cheating, and washed and packed in casks for export.

BELGIAN CONGO (FORMERLY CONGO FREE STATE).

CONGO rubber comes in the shape of buttons, balls (No. 1 and No. 2), red thimbles, and black thimbles. The ball is similar to Cameroons, but tougher. The Dutch Congo ball is the same as the Congo ball, but is known as the best grade of that rubber. There is also the Congo (Kassai), black twist (graded as fine, mixed, and secondary), and red twist. The strips are among the toughest of African rubbers and are dry, with a woody smell.

From the Lower Congo comes also the *Luvituku*, which is a red ball rubber, and from the Upper Congo, the following:

UPPER CONGO.—Ball, red ball, twists, and strips, all of which are good tough rubber.

UELE.—Strips, usually heated and fermented and bad smelling; cakes, wet, but clean.

SANKURU.—Ball, very similar to Congo ball.

LAKE LEOPOLD.—Graded as sausage and ball. It does not differ from the foregoing enough to warrant special description.

EQUATEUR.—In the form of balls (small and mixed). It is dark, dry, and clean, but contains some fermented rubber, which smells badly.

LOPORI.—Graded as ball (large and small), strips, and cakes. Some of the balls are fine and clean, while others contain fermented milk. Lopori also comes as sausage.

BANGUI.—Comes in the form of strips, firm and tough.

BUSSIRA.—Ball; a trifle softer than Lopori, but usually of excellent quality and dry. In use it develops a strong smell.

ARUWIMI.—Ball. This usually comes as large, firm balls. When opened much of the interior is found fermented.

MONGALLA.—In this the ball is similar to Upper Congo red ball. It also comes in strips, and is a good rubber.



Some other designations of Upper Congo are *Kassai*, *Katanga*, *Ikelemba*, *Loango*, *Isanga*, and so on.

BUMBA.—Ball; *Buki*.—Ball; *Tava* and *Kwilu* are all good Upper Congo grades that are not distinctive enough to dwell upon.

WAMBA.—This is a grade of thimbles and is a good black rubber, with only ordinary shrinkage.

#### ANGOLA.

BENGUELA.—Graded as sausage and niggers. Of the latter, No. 1 is clean and tough, and No. 2 contains a large percentage of red leaf.

MOSSAMEDES is practically the same, from a neighboring port.

LOANDA.—In this the grades, which are sausage and niggers, are similar to Benguela, but not so dry. There are also twists (red and black).

AMBRIZ.—Chiefly thimbles or nuts; both are poor grades.

#### EAST AFRICA.

UGANDA rubber comes from British East Africa. It is prepared in sheet form under modern methods, and arrives in good condition.

MOZAMBIQUE rubber is that coming from the port of Mozambique, from other ports in Portuguese East Africa, and perhaps from still other places in East Africa. It possesses some properties in common with the Madagascar rubbers. The rate of shrinkage is less than in most African sorts, and good prices are obtained. In the Liverpool market, which is the best for Mozambique grades, quotations are made for orange ball No. 1, ball No. 2, ball No. 3, liver, sausage, root, sticks or spindles, sticks removed, unripe.

*Orange Ball* (resembling an orange in size and shape) is the choicest rubber. Other grades of Mozambique ball are distinguished further as "white" and "red," the latter being inferior. Its reddish color is due to the fine bark mixed with it. The unripe contains more bark than rubber, and is not thoroughly cured.

*Sticks* or *spindles* consist of spindle-shaped pieces made of slender strings of rubber wound around a bit of wood. Liver (or cakes) is in smooth pieces of irregular size.

LAMU ball, liver, sausage, and root come from the Mozambique port of that name. They are not rubbers of a distinctive sort.

#### MADAGASCAR.

MADAGASCAR rubber formerly ranked higher in price than most other African sorts, though today the highest price is obtained for some of the Congo sorts. Considering the greater loss sustained in washing, it costs nearly as much at times as fine Para. It is a favorite with manufacturers of hard rubber, on account of the fine lustrous polish which it assumes under the buffing wheel. The principal classification is between Pinky and Black.

*Pinky* comes in round balls, weighing  $1\frac{1}{2}$  to 4 pounds, black on the outside from exposure to the air, but having a pinkish-white look when cut.

*Black*, also in small balls, when cut shows a dark color, and is more or less sandy and dirty.

TAMATAVE being the principal seaport, its name is liable to be applied to any grades shipped from there. But what is described as "Prime Pinky Tamatave" is the best Madagascar rubber.

MAJUNGA rubber, from the West Coast town of that name, is a dark rubber of special excellence, ranking next to Pinky in price.

*Niggers* (or negroheads) are designated as "East Coast" and "West Coast," and also as "red ball," and "gristly." They generally contain sand and dirt.

*Brown cure* (or brown slab) is a still lower grade.

*Unripe* is the lowest. This term is applied to balls containing bark in the center.

Rubber from Madagascar is sold at French auctions also as "Lombiro," the native name of a newly found plant, "Morondava," "Barabarja" (names of localities), and so on.

Madagascar rubber is cured (1) by the use of salt water, in which case the water is never wholly expelled, leading to a heavy rate of shrinkage, and (2) by artificial heat. The island is rich in rubber forests, but the exports are restricted by the

wasteful methods of the natives, which exhaust the trees and vines, particularly near the coast.

#### EAST INDIAN RUBBER.

ASSAM rubber, the product of the *Ficus elastica*, is strong and of firm texture. It is fairly elastic, though often less so on account of carelessness in gathering and the introduction of impurities. There are four grades usually (No. 1 to No. 4), of which the lower ones are extremely dirty and contain soft rubber. The better grades when cut have a glossy, marbled appearance, somewhat pinkish in color. Assam rubber is marketed in small balls, made by winding up strings of rubber dried on the trees, and also in oblong slabs of irregular size, wrapped in plaited straw. The output has declined for several years. Meanwhile the same species has been found in Burma, where the production of rubber has increased, though the whole output of forest rubber from British India is now smaller than at an earlier period.

RANGOON rubber is the product of Burma, exported through the port of Rangoon, and differs so little from Assam rubber as to require no separate description. Four grades are marketed, at practically the same prices as for Assam rubber.

JAVA rubber, from the island of this name, is dark and glossy, of a deeper tint than the Assam sorts, with occasional red streaks. Otherwise, its history and characteristics are nearly identical with those of Assam rubber. Three grades are recognized. The milk dries on the surface of the trees, on exposure to the air, and the shrinkage of the better grades is slight.

JELUTONG.—See Pontianak.

PENANG rubber (from one of the states in the Malay peninsula, including the island of Penang) is also very similar to that from Assam. There are three or four grades, at slightly lower prices than the Assam sorts bring.

BORNEO rubber ranks below the other Asiatic sorts, being lower in price, with a higher rate of shrinkage. It is of a whitish color, changing with age to a dull pink or red. It comes to market shaped like pieces of liver, and is soft, porous, or spongy. The pores are filled with salt water or whey, for the

reason that salt is used to coagulate the rubber, and the water evaporating leaves a saline incrustation in the cells. There are three grades, the first of which is a good rubber, while the lowest, when cut, is almost as soft as putty, and is worth little.

PONTIANAK, also known as jelutong, gutta jelutong, Gambia, besk and fluvia, is a low-grade rubber, chiefly from Borneo. It is the product of the latex of the *Dyera costulata*, and as gathered by the natives is doped with kerosene and earthy matters, still further lowering its value. The gum was formerly classed with low grade guttas, as it was often used by the Chinese to adulterate the high-grade guttas. It is, however, not a gutta but a very resinous rubber. The rubber content is about 10 per cent. and when crude rubber was high it was extracted at a profit and hundreds of tons of it used.

There are several grades, as Palembang, Pontianak, Sarawak, Bandjermassin, etc., the names being taken from the districts in which the gums are gathered.

PRESSED OR REFINED PONTIANAK in its naming indicates sufficiently its characteristics. It contains less of the usual impurities, has no odor of kerosene, and on washing and drying loses from 40 to 50 per cent. It brings 6 or 7 cents a pound more than the ordinary grades.

GUTTA-PERCHA.—See Chapter XX. The highest grades, of which there are several, are well typified in what is known as red Macassar, which brings \$2.00 a pound, as compared with the low grades at 19 and 24 cents. The following are low-grade guttas:

GUTTA-SIAK (also called book gutta).—This is a low-grade gutta sometimes mixed with jelutong. It is prepared at Siak in Sumatra and its port of shipment is Singapore. Its regular form is a square folded sheet, or "book" with rounded edges, made by laying a sheet of the softened material in a series of folds, meeting in the center. The final end folds, at right angles to the first, producing the round-edge square book.

Cold gutta-siak cuts tough, gummy and wet and may be cracked or split off by a light blow. The fracture shows a closely laminated mixture of pinkish gutta and white jelutong, giving a fibrous appearance. The fracture is interspersed with specks of

reddish bark. The odor of gutta-siak is slightly earthy. The usual impurities include moisture, bark and clayey earth. The loss on cleaning and drying is about 20 to 25 per cent. The clean gutta is firm and tough with some elasticity and is dark in color with a slightly reddish hue. Siak is like Souni.

GUTTA-COTIE, exported from Singapore. This is a low-grade gutta of somewhat higher grade than gutta-siak because it does not contain an admixture of jelutong. It is prepared in sheets, rolled three inches in diameter, cut into approximately one-foot lengths. It is somewhat less barky than gutta-siak. The shrinkage is about 15 per cent. Normally the market price of gutta-cotie is about 30 per cent. higher than that of gutta-siak.

GUTTA-PENANG.—In the ascending scale, gutta-penang (exported from Singapore), stands next above gutta-cotie in quality. It is prepared in rolled sheets, five or six inches in diameter. The rolls are cut lengthwise and crosswise into pieces about six or eight inches long to expose the interior for inspection. The color is strongly pinkish, slightly specked with bark. The quality and price are practically that of gutta-cotie.

SOUNI is made up of Gutta Derrian, *Dichopsis oblongata*, 2; Gutta Sundeck, *Payena Lerii*, 3; Gutta Pouteh, *Bonha-balen*, 1.

#### OCEANICA

NEW CALEDONIA rubber comes in cakes weighing from 13 to 22 pounds. It is brown to black in color; very pure, slightly smoky. The amount of shrinkage is 18 to 20 per cent.

#### PLANTATION RUBBER.

IN the first edition of this work two lines seemed enough to devote to plantation rubber, since so little had then appeared in the market. In fact, with the exception of a few scientists and a smaller number of enthusiastic planters, no one at that time seemed to regard rubber cultivation as a practical proposition, and the rubber manufacturers were not the least prejudiced against undertakings in this line. Now, however, 81 per cent. of the world's supply of rubber is derived from plantations. Since 1900 the world's annual production of crude rubber from all sources has increased from 54,000 tons to 270,000 tons. The leading factor underlying this rapid growth is



the extensive use of rubber for motor-vehicle tires. The extra rubber came almost wholly from plantations.

Production of Plantation Para rubber is also established on a scientific basis. Every phase of its cultivation and production proceeds under the close study and carefully planned experiments of government and plantation association experts. The measures have practically attained the economical production of standard Para grades capable of supplanting the best wild Para for essentially every purpose.

The prediction was made in 1909, by the planting interests of the Far East, that when the *Hevea* trees then planted should reach tappable size, Ceylon and Malaya would alone produce as much rubber as at that date entered into the world's total consumption. This result was attained in 1914. The growth by years is interesting.

Year	Pounds	Year	Pounds	Year	Pounds
1903 .....	47,040	1908 .....	4,032,000	1913 .....	106,664,320
1904 .....	96,320	1909 .....	8,064,000	1914 .....	159,891,200
1905 .....	324,800	1910 .....	18,368,000	1915 .....	241,622,080
1906 .....	1,142,400	1911 .....	32,298,560	1916 .....	341,936,000
1907 .....	2,240,000	1912 .....	63,881,320	1917 (est.).	492,800,000

Any fear of overproduction of rubber, through the coming into bearing of so many planted trees, is offset by the fact that thus far the sources of wild or forest rubber, with the sole exception of the native *Hevea* (Para) trees in Brazil, are being exhausted by the extraction of their product. Where trees and vines are killed by the rubber gatherers, there may be an increased yield from a given country for a while, due to the working of new areas from time to time, but ultimately the principal forests are overrun, after which the output falls off.

The cleanliness of plantation as compared with forest rubber has been an attraction from the beginning, and the higher price paid for the former has been due to its greater content, bulk for bulk, of rubber. Originally it proved deficient in strength as compared with the Brazilian product. For some purposes the deficiency of nerve of the new rubber did not prove a disadvantage, as, for instance, in solution making, in which it has been largely used. Gradually, however, it has replaced Para in practically every use to which the wild gum is put.

Rubber from *Hevea* plantations was at first clearly not identical with the product of the same species under forest conditions. The question was discussed as to whether this difference was due to the plantation rubber not being smoked, as is done with Brazilian rubber. A reason now more generally given is that, owing to the tapping of planted trees having been begun at a very early age, the product was "immature." At least plantation rubber can now be had with more strength than formerly, which may be due either to increased age of the trees or to better methods of collection, coagulation, and care in subsequent storage and shipment.

PLANTATION OR PLANTATION PARA is the term applied in the trade to the new class of rubber. "Ceylon," "Malaya," "Straits," "Java," and "Sumatra" are also applied, but these are merely local designations, indicating no difference in quality, all being produced by cultivated *Hevea*. What is more important is the growing practice of planters of stamping their product with trade-marks, by means of which buyers may know absolutely the source of any particular purchase, which is helpful when a producer of several tons in a year is attempting to establish a reputation for quality. Plantation Para is produced in various forms, as follows:

*Biscuits*.—Prepared by allowing the rubber milk to set in shallow receptacles, with or without acetic acid, and washing and rolling the cake of rubber which appears at the top more or less circular in form—usually  $1/16$  to  $1/8$  inch in thickness and 10 to 14 inches in diameter.

*Sheets*.—Formed in the same way as biscuits, but rectangular in outline. On account of their shape they lend themselves to more economic packing. Biscuits and sheets are sometimes pressed together to form blocks.

*Crêpe*.—This rubber, on account of the washing and tearing which it undergoes between the rollers of the washing machine used in its preparation, contains a minimum of impurities. It has an irregular surface, is uneven in thickness, and, like lace or flake rubber, dries rapidly. On account of the washing which some manufacturers subject all rubber to, it has been questioned whether the extra labor involved in its preparation will be paid

for by the extra price realized. Prepared in lengths of 3 to 6 feet, and widths of 5 to 12 inches, and graded according to color.

*Worm.*—The product obtained by cutting irregular sheets of freshly coagulated rubber into thin worm-like rods, shears or machinery being used. By passing the dry worms through ordinary washing rollers they are bound together into an even strip of crêpe.

*Lace.*—Very thin perforated sheets of considerable lengths. It comes from the machine in a continuous strip, and is cut into pieces 6 feet long as it runs on to wire trays. It is sometimes pressed later into biscuits or sheets.

*Flake.*—Obtained by placing small pieces of freshly coagulated rubber in a small rolling machine or washer, the corrugations of which run horizontally; the rollers are close together and the cut rubber issues as thin strips.

*Block.*—Made from pressing together sheets, biscuits, or other forms of rubber, in a freshly coagulated or partly dry state, in sizes usually 10 x 10 x 6 inches, the chief purpose being to reduce to a minimum the surface exposed to the air after preparation.

*Scrap.*—The remnants obtained after tapping, rolled into balls or made up into cakes. It is shipped with or without other preparation; it is sometimes made into crêpe. It brings a comparatively high price.

Of these various forms the present accepted types with their market names are:

**FIRST LATEX CREPE.**—A thin, pale, and clean crêped sheet, the best grade of Plantation Para.

**AMBER CREPE.**—This comes in four grades, described as "gristly blanket." It is rough, thick, and light-colored. The other grades are similar in form but vary in color to dark amber, frequently mottled in appearance.

**BROWN CREPE.**—A lower grade than amber crêpe, varying from thick to thin sheet; light to dark-brown color. Frequently it is specky with barkly impurities, requires washing, and is easily torn apart in the sheet.



SMOKED SHEET, RIBBED STANDARD QUALITY.—This form has the distinctive smoked Para odor, varies in color from light to dark-brown, and viewed by transmitted light, is translucent. It strongly resists stretching and may be distended into a thin film exhibiting marked tensile strength and stretch. The surfaces are embossed with various designs of ribbing, sometimes including plantation names. These designs serve as trade-marks for the identification of the produce from individual plantations.

SMOKED SHEET, PLAIN STANDARD QUALITY.—This is the same in all respects as the “ribbed standard quality” except that it has no ribbing.

UNSMOKED SHEET, STANDARD QUALITY.—The same as plain smoked sheet except unsmoked.

COLOMBO SCRAP.—Massed clear, light-brown strings and bits of high-grade rubber, more or less specked with bark.

CEARA plantation, from *Manihots*, comes from Ceylon and Malaya, and from some German colonies in Africa.

MEXICAN plantation is very clean, not differing otherwise in quality from the product of the same tree (*Castilloa*) under forest conditions. It comes as strips, when the latex is creamed, coagulated, and run between rolls, and as Grena when the product is scrap-picked from the cuts on the trees and coagulated only by exposure to the air.

TRINIDAD plantation, TOBAGO plantation, WEST INDIES plantation, CENTRAL AMERICAN plantation, GUAYAQUIL “*Castilloa*,” and such terms relate to the product of cultivated *Castilloa* trees in the regions indicated. A certain amount of *Castilloa* plantation rubber also comes from Ceylon and Java.

CONGO plantation, from various species, comes from Belgian Congo (Congo Free State).

UGANDA plantation comes from British East Africa.

RAMBONG is the native name in the Far East for the *Ficus elastica*, which produces the Assam rubber of commerce. A considerable amount of cultivated Java and Ceylon *Ficus* rubber is sold under this name. This comes in crêpe, sheet, and block.

## CHAPTER II.

### SOME LITTLE KNOWN RUBBERS AND BASTARD OR PSEUDO GUMS.

FROM time to time reports come in from all over the tropical world regarding the discovery of gums, some of which are similar to india rubber, while others are more like gutta-percha. In a few instances these gums have appeared on the market, in due time, under various names and have been useful. This is not the rule, however, and it is due to a variety of reasons. The first is the scientific attitude of those who primarily examine the samples received at the great centers of civilization. Unless gums are of high grade, and bear promise of being nearly as valuable as a good grade of india rubber or gutta-percha, they are usually pronounced worthless, or nearly so. Nevertheless, rubber manufacturers are ever in the market for these products, and would welcome many of the pseudo gums and find large uses for them, if once they were within reach.

Aside from the scientific attitude is the indifference of the gatherers in their native wilds, of the importers who see little profit in such cheap gums, and of the manufacturers themselves, who wait until a neighbor has tried something new before venturing to experiment.

One has only to recall what is needed in rubber compounding to see how valuable many of these gums could be made. For example, sometimes simple stickiness is called for, in another case only insulating qualities and stickiness, in still another, water-proofing qualities and stickiness, and, it is well to add here, where only one valuable quality exists in a gum others can often be supplied. As a matter of fact, in the present state of compounding and manipulation, the presence of resins is not heeded, short life can be overcome, and intractability can be done away with.

It is with the hope that some of the gums mentioned in the following pages may be useful in rubber manufacture that space has been given to them.

ABBA RUBBER.—This is from Lagos, probably the product of the *Ficus Vogelii*. It is low grade, cures soft and short, and contains a large percentage of resin. The trees are most abundant in Grand Bassam, and grow rapidly to great size, single trees often yielding 10 or 12 pounds in a season. The milk is coagulated by adding vegetable acids and boiling. The rubber is bright red. It contains about 55 per cent. rubber and 45 per cent. resin, and forms 30 per cent. of the latex. The washing loss is 10 to 14 per cent. One report is that the latex of this tree is mixed with that of *Funtumia elastica*, the mixture being called by the natives "aba-odo."

ABYSSINIAN GUTTA.—An adhesive acid gum of an earthy brown color, similar to common gutta in external appearance. Softens in water, but keeps a very great elasticity. On drying it remains exceedingly adhesive, therefore could not be used in place of gutta-percha, but with proper treatment would undoubtedly make an excellent friction gum.

ALMEIDINA.—This comes from West Africa, particularly from the Cameroons and Angola, and has been found in the Solomon Islands. Its source is a shrub with succulent stems, all of which are tapped. The milk is boiled and the resultant balls dried in the sun. It comes to market in small and sulphur-colored nodules, resembling potatoes, for which reason it sometimes has been called "potato gum." When broken open, these balls look like putty, and although quite brittle when cold, the gum easily softens in warm water and may be drawn out in threads, which are possessed of some elasticity. It is completely melted at 240 degrees F., and remains rather sticky after melting. It almost completely dissolves in cold benzine; in fact, nearly all of the solvents ordinarily used in rubber manufacture dissolve it. It mixes and dissolves with rubber in almost any proportion and up to 25 per cent. at least. Not only does it not injure the rubber, but is said to be beneficial to it. In working on the mill a pungent vapor arises from the mass, which, however, has no poisonous effect.

In using this gum, a little caustic soda sometimes is added to the water when it is being washed; some manufacturers add tannic acid. Animal or vegetable fixed oils do not dissolve Almeidina, and therefore when mixed with it are apt to rot it. Mixed with gutta-percha this gum is practically indestructible. The name "Almeidina" is that of the first important shipper of the gum; in England the spelling "Almadina" has come into use. The gum is known also as "Euphorbia gum." Warburg and Jumelle say that Almeidina comes from *Euphorbia rhipsaloides*, which must not be confused with *E. tirucalli*. Berry gives Almeidina 82.78 per cent. resin, and 9.40 per cent. hydrocarbon.

Latex from *E. lactiflua* (Chili) contains 3.88 to 5.00 per cent. of caoutchouc and 31.9 per cent. resins reckoned on the dry substance.

AMAZONIAN RESIN RUBBERS.—The valley of the Amazon contains various trees and plants that are caoutchouc producers, but which are generally neglected, as the gatherers are seeking the more valuable *Hevea* or *Castilloa*. At the same time the latex of some of these plants has been referred to as being used to a considerable extent for adulterating Para rubber. Among these are mentioned the trees known under the native names of Amapa, Sucuba, Surva, Tamanguiro, Molango, etc. All of these show a marked percentage of resin in the milk.

ANTIPOLO GUM is being made from *Artocarpus incisa* (the breadfruit tree) in the Philippines. Antipolo is a town in the province of Luzon.

BAKA GUM.—Found in the Fiji archipelago. Comes from *Ficus obliqua* (Foret). Used by natives for birdlime. Milk very abundant. Gum little known. Samples sent to England were reported upon as being suitable for mixing.

BANANA RUBBER.—Green bananas yield considerable latex, which is 95.7 per cent. water and only 3.9 per cent. rubber. It is easily coagulated by boiling. Made from *Musa sapientum* and *M. paradisiaca*.

BARTA-BALLI.—One of the best known native trees in the Guianas. The milk of this tree is sometimes mixed with Balata milk and is said to give it its reddish tint. The gum when dried

by evaporation is rather sticky and soft, but when precipitated in alcohol is dry and firm. Reports from England are rather condemnatory as the gum is said to absorb a great deal of water in washing, which it retains very obstinately. The same gum, dried by precipitation by spirits of wine, is said to be very brittle. Known also as Cumaka-balli.

BEIRA RUBBER.—Another name for stick rubber, gathered on the East Coast of Africa, and shipped from Beira.

CANOE GUMS.—From the bark of the breadfruit tree, which is found so plentifully in the islands of the Indian archipelago, comes a thick mucilaginous fluid which hardens by exposure to the air. When boiled with coconut oil it makes a tough, rubber-like substance, wholly waterproof, and very lasting. It is used ordinarily for waterproofing seams of canoes, pails, etc. It is also used when fresh, as a birdlime. Is probably from the *Artocarpus integrifolia*.

CATTIMANDU GUM.—Derived from an *Euphorbia* found at the Cape of Good Hope. The juice is so acrid as to give intense irritation to any part of the body with which it may come in contact. The gum has been used as an anti-fouling dressing for ships' bottoms, but is little known otherwise.

The natives use the milk as a cement to fasten knives in their handles. Under the influence of heat it becomes soft and viscid and when dry is very brittle. It is probably about as useful as Indian gutta. Found in Vizagapatam, India. Cattimandu gum seems to be from *Euphorbia trigona*.

CATIVO GUM.—This comes from a tree called "Cativo" found in Central America and the United States of Colombia. The gum is fluid at 130 degrees F., and if the temperature be raised to 212 degrees F. it is easily filtered, impurities are removed, and a somewhat objectionable smell is greatly lessened. The gum is then of a clear reddish-brown color. It mixes easily with rubber and is said to produce a very tough compound. When vulcanized with 5 per cent. sulphur, this gum makes a fine, elastic product. When vulcanized with more than 5 per cent. sulphur, it becomes like gutta-percha, and can be sheeted or molded, when warmed.

CHICLE.—A gummy, resinous substance found in the *Achras sapota*, a tree growing abundantly in the warm, damp regions of



Mexico, and also in portions of Central America. Chicle should be of a whitish color, odorless, and free from impurities, but often is adulterated with an inferior pink or reddish soil. It is solid and brittle at ordinary temperatures, but becomes plastic when placed in hot water. It is quite soft at 49 degrees C. (120 degrees F.). It is used chiefly in the United States in the manufacture of chewing gums, and to a small extent in England for adhesive plasters. It has been used for modeling purposes and for mixture with india rubber for insulation work. The fruit is about as large as an apple, though looking more like a quince and is eaten under the name of "sapodilla" or "sapotilla" plum. The fruit is pricked or sliced and the latex is allowed to ooze out without squeezing, so as not to get the other juices. Lateral tapping is used on the tree, and 15 to 25 pounds of milk or 5 or 6 pounds of gum may be obtained in one season without injuring the tree. The milk is coagulated by boiling. Prolonged boiling makes it reddish, though some trees are said to yield a red gum. The best chicle is made from highland grown trees. The trees sometimes grow 70 feet high, and the wood, which is very heavy, takes a high polish and is quite valuable. The analysis of chicle shows 44.80 per cent. resin, 17.20 per cent. rubber, 9 per cent. water, and 8.20 per cent. starch and other matters, on an average. It sometimes contains as much as 55 per cent. of resins when dry.

Chicle is 60 per cent. soluble in acetone; the remainder can be powdered and has none of the characteristics of rubber.

COORONGITE.—Sometimes known as Australian caoutchouc. An india-rubber-like material, discovered first near Salt creek, a short distance from the coast of South Australia. It was first observed in little hollows of sand and resembled patches of dried leather, but it generally occurs in the swamps. It is supposed to be of the petroleum series. Some scientific authorities in England and America ascribe to it a vegetable origin and regard the gum as exuding from a plant or lichen. It is not soluble in the ordinary rubber solvents, but after mixing with india rubber it can be dissolved. According to Forster, it vulcanizes somewhat as india rubber does.

COW TREE RUBBER.—The cow tree is very plentiful in tropical South America and yields a milk commonly used for food. This milk contains considerable caoutchouc, which is about 30 per cent. resin. Botanically it is known as the *Brosimum galactodendron*. Besides *Brosimum galactodendron*, Warburg mentions another cow tree, *Couma utilis*, an *Apocynaceæ*, growing in northern Brazil, while *B. galactodendron* is an *Artocarpa* of Venezuela. *Couma utilis* latex contains rubber, and is used by the natives in waterproofing. Cow tree milk is exceedingly hard to coagulate, and evaporation product is completely soluble in hot acetone, seeming to indicate absence of any rubber. The constituents are mainly fatty matter, possessing neither tenacity nor elasticity, according to the German chemists.

CUMAI RUBBER.—From the milk of a tree found on the Rio Negro and Uaupes, in Brazil. None comes to market. This milk is used by the natives for waterproofing purposes.

GOA GUM.—This is a gum that comes from the Mivalcantiem, which grows wild in the Coucan district in Brazil, and is also planted for hedges. Chocolate in color, softens under heat, is easily molded, and thoroughly waterproof.

GUTTA-BASSIA.—Found between Upper Senegal and the Nile. Has the appearance and apparently many of the properties of gutta-percha. Softens in warm water and becomes glutinous at the boiling point. Is soluble in sulphide of carbon, chloroform, benzole, and alcohol. Can be kneaded in water as easily as ordinary gutta. It may be the same as Karite gutta, which is from *Bassia Parkii*, though there are other African Bassias which are said to yield good gutta.

GUTTA-GREK.—A gum that comes from Palembang, in Straits Settlements. It appears very much like india rubber but is permanently softened and destroyed by heat sufficient to melt it. It smells like gutta-percha rather than india rubber.

GUTTA-HORFOOT.—This is a vegetable juice sent in sealed tins from the Straits Settlements, which yields a material like india rubber of fair quality. No way of coagulating the juice, where it is gathered, seems to be known.

GUTTA-SHEA.—Said to be the nearest approach to gutta-percha among African products; obtained from the Shea,

Galam, or Bambouk rubber-tree (*Butyrospermum Parkii*). The butter is the solid fat contained in the seeds and is used in making hard soaps. Gutta-shea is separated from the fat in the course of the soap making and is found to be present to the extent of from 5 to 75 per cent. A kind of gutta-percha is also obtained from the trunk of the tree in small quantities. Also known as "Karite gum." Analysis of the butter shows: guttalike 25.20 per cent.; resin 57.13 per cent.; water 5.04 per cent.; impurities 12.63 per cent. The yellowish butter smells and tastes much like cocoa butter. Casalbo claimed to have differentiated two varieties, one yielding a red and the other a yellowish gum. The red kind is the more valuable, and this tree also yields gum from its trunk, while the yellow gum tree does not. It is uncertain whether the yellow butter yields any gutta, though the trunk gutta from the other variety is comparable to Red Borneo in toughness and in its structure. Called also "Karite gutta" and "Shea butter." Knowledge on this subject is still confused and the authorities conflict. The two varieties are called "Shea" and "Mana," the Shea being the one which yields gutta, and also the more abundant variety. The branches seem to yield even more than the trunk. The milk is allowed to stand in the open air for about 24 hours, when it partially curdles. The crystalline particles are then kneaded into a mass in hot water. However, reports on this gum are conflicting, and it is probable that two sources are confused. Some advices seem to point to the plumb-like fruit as the source of both gutta and butter. Fendler and Heim consider Karite gutta worthless as a substitute for gutta-percha.

GUTTA-SUSU OR BORNEO No. 3.—Also called "gutta grip," at Singapore, and formerly known as "Assam white." The washing loss is 30 to 45 per cent., and the clean rubber contains 14.5 per cent. resin. In Java and Sumatra it is generally stored under water. The vine is tapped and the gum left to dry on the bark. The milk is sometimes gathered and coagulated with salt and boiling, but this method is not so good as bark drying. It is white and remains so under water, but darkens on exposure to the air.



INDIAN HEMP RUBBER (*Apocynum*).—Coagulation of latex is spontaneous, yielding about 33 per cent. of coagulum, containing 4 per cent. of low-grade, black, soft rubber.

JELUTONG.—See Pontianak.

JEVE, JEBE, OR HEVE (hence *Hevea*) was the ancient name for rubber among the natives of Ecuador. The name was applied to a rubber coming principally from the neighborhood of Iquitos, Peru. (See Peruvian rubber.)

JINTAWAN.—A bastard gutta-percha mentioned by Thomas Hancock in four patents and also by Taylor and Duncan. Probably a mis-spelling of "Djintaan soesoa," the same as gutta-susu.

LORANTHUS RUBBER.—A sticky non-elastic Venezuelan product. Contains 18 per cent. of resin.

MABOA GUM.—Said to be produced from a species of *Ficus* in Santiago de Cuba.

MACWARRIEBALLI GUM.—A rubber gathered in British Guiana from the *Forsteronia gracilis*. From the report of the director of the Kew gardens, to whom a sample was submitted, it would seem that, while the gum is at present unfit for use in place of ordinary caoutchouc, because of its stickiness, it might be of value in cements, frictions, and the like. *Forsteronia gracilis* is a vine or bush rope belonging to the *Apocynaceæ*. The milk appears to be often mixed with that of balata or Bartaballi, though Macwarrieballi is more like rubber than balata. The vine is very rich in latex.

MANGEGATU GUM.—This comes from Vizagapatam, India, is a gum of the bastard gutta type, and is said to come from the *Ficus Indica*.

MANDARNVA RUBBER.—A low grade of South American gum, somewhat like Ceara rubber. Little known. Is said to grow on the dry arid uplands of the interior. Is one of a number of gums that bear the native names, "Cauchin," "Pau," and "Massaranduba."

MANGA-ICE RUBBER.—Argentine republic. It is very abundant. Produces good rubber.

MUDAR GUM.—This comes from an *Asclepiad*, commonly known as gigantic swallowwort (*Calotropis gigantea*). The

shrub is found throughout the Southern provinces of India and grows to a height of from six to ten feet. Produces a gutta-like substance, which becomes plastic in hot water, and in other ways acts somewhat like gutta-percha. It insulates badly, but is recommended for waterproofing. Analysis: Rubber, 16.92 per cent.; rosin, 83.08 per cent., according to Warden (1885). Hooper found 25.54 per cent. of a rather poor rubber, and 62 per cent. resin.

MUSA GUM.—A gum expressed from the peel and leaves of the banana and pisang plants. No gum yet on the market. Process patented in England by Otto Zurcher, of Kingston, Jamaica. Also called "banana rubber" (which see).

NAMAQUALAND RUBBER (*Euphorbia drageana*).—A new source of rubber growing wild in the uplands of Namaqualand, South Africa. It is said to yield 17.6 per cent. pure rubber and 70 per cent. resin.

NEEN RUBBER.—A rubber-like gum said to be produced by an insect, reported from Yucatan. The insect belongs to the coccus family, feeds on the mango tree, and swarms in those regions. It is of considerable size, yellowish brown in color, and emits a peculiar oily odor. The body of the insect contains a large proportion of grease, which is highly prized by the natives for its medicinal properties in skin diseases. When exposed to great heat, the lighter oils of the grease volatilize, leaving a tough wax which resembles shellac. When burnt this wax produces a thick semi-fluid mass, like a solution of india rubber. An "ant wax" or lac is found in Madagascar and is secreted by two insects, *Gascardia Madagascariensis* and *Gascardia Perrieri*. The former secretes a white gum, containing 52 per cent. of resin. The latter secretes red gum, with 46 to 48 per cent. resin. The two gums have the same value.

OCOTILLO RUBBER.—A plastic extracted from the ocotillo plant (*Fouquieria splendens*), a shrub common to Texas, Arizona and Northern Mexico.

PALA GUM.—Found in Assam and Ceylon. The wood and the bark are valued in India for their medicinal qualities. The tree yields an abundant milky juice, which after coagulation

acts something like gutta-percha. It readily softens in hot water and takes impressions, which are retained when cold. Also known as "Indian gutta-percha." Comes from the *Dichopsis elliptica*. It has been used as an adulterant of Singapore gutta for some years. It was used also as birdlime or cement and keeps well under water. Is hard and brittle when cold. The resin is easily removed by boiling alcohol, and the residue appears to be a very fair gutta.

PALO AMARILLO.—A varnish-like gum from the latex of the Mexican tree *Euphorbia fulva*. Analysis of the latex gives 34 per cent. gum and 6 per cent. resin. So far the gum is not susceptible of vulcanization and is not elastic.

PALO COLORADO.—A Mexican grade derived from the tree known as *palo colorado* in the state of Durango.

P. F. U.—A good rubber, not now obtained commercially, the source of which was the Colorado desert weed, the *Picramnia floribunda utilis*.

PICKEUM GUM.—See Guayule.

SARUA RUBBER.—Found in the Fiji archipelago, from *Alstonia plumosa*. Formerly collected largely, but little comes now to the market. Natives take no interest in its collection. The juice comes from the stems and leaves but not from the trunk of the tree. It is soft at first but coagulates almost at once, hardens after a time, and becomes inelastic, of about the color and consistency of putty. It is gathered by the natives during a season of three months.

SEIBA GUM.—See Tuno.

SUSU-POKO (meaning English tree milk).—A gum from a tree growing in the Malay peninsula, used in the place of gutta-percha, after being cleansed and treated with chloride of sulphur. Mentioned by Leonard Wray in 1858.

TALOTALO GUM.—Found in the Fiji archipelago. Comes from *Tabernaemontana Thurstoni*. The gum is hard, gutta-like, and without elasticity. Also called "Kau Drega." The milk is thin, but the tree grows large, up to two feet in diameter, and it is the best rubber source in the Fiji islands.

**TALAING RUBBER.**—An almost black rubber which, when cut into, is white and porous, presenting a honeycombed appearance, the cavities being filled with a watery fluid. It is quite tough and elastic and appears to be of good quality. It comes from a creeper which is abundant in the Philippines, in Malacca, and Indo-China. The juice is very abundant, and is coagulated by being boiled in water.

**TIRUCALLI GUM.**—This is a *Euphorbium* gum, from the Indian plant known as milk hedge. The milk of this plant is used for various purposes, chiefly medicinal, in India, and has been suggested as a substitute for gutta-percha. Like gum *Euphorbium*, it has a very acrid character, and the collection of it is a very dangerous operation to the eyes. When dry it becomes very brittle, but when warmed in water is quite elastic.

**TOUCHPONG GUM.**—It is found throughout the Guianas. Probably from *Sapium biglandulosum*. Spelled "touchpong" by Jenman; "touchpong" by Morris; "pouckpong" by Dr. Hugo Miller. The rubber dries in strips on the trees, and what little of it comes to market has not been recognized as a distinct sort. Samples sent to England, however, have been favorably reported on.

Analysis of touchpong gum by the Imperial Institute, London, gave 93.7 per cent. rubber and 1.8 per cent. resin.

**TU CHUNG RUBBER.**—This is an interesting gum derived from the *Eucommia ulmoides*, or the chung tree, native of China. It has been definitely established that this tree can be readily acclimated in temperate countries.

**TUNO** is a trade name applied to a gum gathered principally in Nicaragua and Honduras. It is the product of what has been called the "sterile rubber tree" and also the "male rubber tree" of Nicaragua. The milk is coagulated with the aid of heat. The gum is but slightly elastic, is very sticky when heated, and is cheap. It is used as a friction gum, and is also mixed with balata in the manufacture of belting. Sometimes it is sold under the name of "Seiba gum," its identity being lost by ingenious massing and manipulation under water. Nicaragua rubber adulterated with "Tuno" in coagulation soon

hardens and loses its elasticity. Also spelled "Toonu" and "Tunu." It is derived from *Castilloa tunu*, and called locally "caucho macho" or male rubber. Though it has a bad reputation, Mr. E. Poisson has drawn excellent rubber from this same tree in Costa Rica. Tuno gum usually runs over 80 per cent. resin. Berry gives it 80 to 86.13 per cent. resin, and 3.50 to 7.06 per cent. hydrocarbons (gutta-like).

YELLOW GUTTA.—This comes from the Sunda Isles, from the genus *Payena*. It is practically a compound of india rubber with two resins. One of these is crystallizable and the other is pitchy. If the raw material be treated with boiling alcohol the resins are taken off and the remaining product appears to be good india rubber. Berry describes yellow gutta as "a gum of dual composition containing the hard resins characteristic of chicle, and the elastic caoutchouc-like hydrocarbon characteristic of rubber." It is more like rubber than gutta. The analysis gave 80 per cent. resin and 12.58 per cent. hydrocarbons (rubber?). The resin looks like chicle resin, and has a saponification value of 104.1, with a trace of acid. However, there are several guttas which are yellow.

## CHAPTER III.

### COAGULATION OF RUBBER LATEX.

WITH the advent of the chemist in the rubber factory an exact knowledge of the various treatments to which india rubber may be subjected in forest or plantation is not only interesting but often of the greatest value. For this reason the following review of coagulating processes and systems is given at some length:

Rubber latex is a mixed suspension and solution of rubber globules, resins, nitrogenous bodies (albumens or proteins), and saline substances contained in a watery medium or serum.

Typical *Hevea* undiluted latex from Malaya (average from 100 ten-year-old trees by Beadle and Stevens).

	Per cent.
Rubber .....	35.62
Resin .....	1.65
Proteins .....	2.03
Mineral Matter .....	0.70
Water .....	60.00
	<hr/> 100.00

The proteins are in colloidal solution and are capable of being precipitated by certain reagents, notably acids. Latex being a combined solution and suspension, has many of the characteristics of a colloidal solution. It seems probable that the protein acts as a protective colloid to the pure caoutchouc present due to the adsorption of a layer of the dissolved protective agent over the surface of each of the suspended rubber particles.

Four well-defined stages in the degree of coherence of rubber separated from latex have been noted by a writer in the "Tropical Agriculturist," namely:

1. Creaming is the condition observed in the early stages of slow coagulation.



2. Flocculence refers to the formation of small particles of rubber without coalescence into lumps. This state is observable in latex to which much formalin has been added.

3. Agglutination, or local lumpy coagulation, observed when latex coagulates spontaneously, or when certain mineral salts are added.

4. Coagulation proper is the final stage observed on careful addition of acids to latex, the rubber forming in one clot and leaving a clear liquid.

The purpose of coagulation is the separation of the rubber substances from the watery or serum portion of the latex. The differences between unlike grades of rubber are due partly to chemical composition, and also in a measure to varying methods of collection and coagulation. It is undoubtedly true that no one method of collection would be best for all kinds of rubber gathered, even if it were possible. It is important to the rubber manufacturer to know what systems are pursued, and particularly what ingredients are added, to produce coagulation, that he may standardize his compounds in respect to rubber quality.

There are four basic methods of coagulating rubber latex:

1. Smoking.
2. Drying.
3. Separation by chemicals.
4. Mechanical separation.

SMOKING rubber is the system with which the world at large is most familiar, and is practised in the Amazonian forests in the collection of Para gum. Several kinds of palm nuts are used to produce a thick smudge, but those preferred are from the Urucuri palm (*Attalea excelsa*). This smoke has been found by analysis to consist mainly of acetic acid and creosote, the latter being a well-known preservative of rubber. Fine Para rubber is nearly always smoked in this way. Coarse Para is air dried. There are also trees found in the forests where it is impossible to get palm nuts, the wood of which is used successfully for the coagulating smoke.

Smoke fumes, in addition to their coagulating action, exert a preservative effect by impregnating the coagulated gum with

creosote and formalin. Coagulation by smoking evaporates a considerable portion of the water contained in the latex. The temperature of the smoke close to the rubber in the native smoking of wild Para is about 160 degrees F.

DRY COAGULATION—HEAT, AIR, SUNLIGHT.—Various rubbers are coagulated simply by the exposure to slight artificial heat, to the sunlight, or merely to the air. Such are the coarse Para rubbers, certain of the Centrals, African, and East Indian rubbers. Fiji rubber is coagulated in the mouths of the natives, and some Angola rubber by evaporation on the arms and breasts of the natives.

Some kinds of rubber dry directly on the tree and are removed in the shape of rubber threads compressed into large lumps or wound. Scrap of all descriptions of rubber is generally obtained in wild and plantation culture through drying, in many cases with the help of chemicals. There is also, in some cases, simultaneous addition of certain decoctions (such as tannic acid, soap, salt, etc.). An important drying process, in conjunction with the use of chemicals is the Leva process, discovered by Dr. Hindorff and used in the production of plantation *Manihot* rubber. In this process the tree is previously coated with the extractive chemical solutions, the bark is next cut with a rounded knife. The latex which exudes coagulates while running down and is gathered from the trunk.

A direct tannin drying process, first defined by A. Schulte, for *Funtumia* (*Kickxia*), is operated as follows:

*Funtumia* latex is poured into a pan and sprinkled with tannin solution. The vessel is shaken and soon the mass can be turned in the mold like a pancake. The uncoagulated side is then sprinkled with tannin and the movement continued. Finally the cake thus formed is squeezed through a wringer to extract the water.

SEPARATION BY CHEMICALS.—Many chemicals exercise a separating influence in the extraction of rubber from the latex. The first collectors of wild rubber used these influences as they exist in the form of smoking and plant juices, as well as in soaps and salts; also in the natural forms of perspiration, saliva and urine.

It was at first thought that the action of acids upon coagulation was only due to the insolubility of the albuminoids containing the globules of rubber. M. Henri has since shown that with latex freed from its salts or crystalloids, acids do not produce complete coagulation, but only the agglutination of the rubber. In ordinary *Hevea* latex all acids produce coagulation, but the proportions of organic acids needed for that result are larger than in the case with mineral acids. The former are preferred on account of the corrosive action of the latter (such as sulphuric, nitric or hydrofluoric acids) upon the impurities which remain in the mass, as well as upon the metallic portions of the plantation factory plants.

With respect to albumen, Dr. Frank concludes regarding chemical means of coagulation:

1. All agents which precipitate and denature albumen operate toward separating the rubber.

2. Separating agents which exercise a decomposing influence upon the accompanying albuminous substance, or lead to its decomposition, require in addition to the coagulating agent, the simultaneous presence of preservatives. Substances which do not exercise such a decomposing effect can be used by themselves.

MECHANICAL SEPARATION.—The real mechanical method for removing the rubber substance from the latex is the centrifugal system by which a centrifugal machine removes the watery contents and produces a marvelously clear elastic rubber. This process is particularly suitable for *Ficus* latex. It also seems adapted for *Hevea* latex, but in the latter case acid should be added previous to the centrifugal action.

A mechanical process of separation used on a large scale in the Dutch colonies, for the coagulation of *Ficus* latex, consists of subjecting the strained latex to the action of a beater or twirling rod. The addition of the thickened, creamy portion from latex which has been standing, materially hastens the separation and renders the process practical.

Another mechanical process is that of Professor Daner for *Castilloa*, in which foreign substances, particularly those of an albuminous nature, are separated by dilution.

The following descriptions embrace the ordinary materials employed for coagulation as well as certain patented machines and processes.

**AMOLE JUICE.**—A native process for coagulating the milk of the rubber tree, which prevails throughout Central America, involves the use of an alkaline decoction made from the juice of a plant called "achete" or "coasso" (*Ipomœa bona-nox*, Linn., and also *Calonyction speciosum*). This is combined with rubber milk in the proportion of 1 pint to 1½ gallons of the latter. During coagulation the vessels are often heated from 165 degrees to 175 degrees F. After coagulation, the rubber is dried for twelve to fourteen days. The kinds of rubber coagulated in this fashion are Mexican, Nicaraguan, and in fact almost all of the rubbers that come under the head of Centrals, and are obtained from the *Castilloa elastica*.

**ACETIC ACID.**—Used in coagulating *Hevea* latex in the Far East. This acid, originally suggested by Perkins in 1898, is now used for coagulation in about 98 per cent. of plantation rubber produced.

**ALCOHOL.**—One of the best general coagulants, but too costly to be commercially available.

**ALUM.**—This is used all through the Isthmus of Panama, and in coagulating Accra rubbers and other African sorts. Pernambuco rubber is also treated with a water solution of alum, as is the Nicaraguan at times.

**BOSANGA.**—The juice of the *Costus afer*, a seed used in the coagulation of the latex of *Landolphia* in the Lopori district in central Africa.

**COCONUT WATER.**—Fermented coconut water has been found to be a cheap, satisfactory substitute for coagulating *Hevea* latex in place of acetic acid.

**COYUNTLA JUICE.**—This is an astringent juice made from the Mexican weed of that name. When the rubber milk is gathered, it is placed in earthenware vessels and whipped with the weed, which causes coagulation. The Mexican rubber known as Tuxpam is treated in this way.

**FORMIC ACID.**—Used instead of acetic acid in coagulating *Hevea* latex.

HELPER PROCESS.—This consists of the addition of a solution of acetic acid, and is based on the knowledge derived from the analysis of the smoke of the Urucuri nuts.

KOALATEX.—A proprietary preparation used in Ceylon and the Federated Malay States for coagulating the latex of the *Hevea Brasiliensis*.

LIME.—A final process in the coagulation of rubber in India is the washing over with lime. Collins also mentions the use of lime in connection with the coagulation of Para rubber.

LIME JUICE.—Lagos rubber and some other African sorts are coagulated by the addition of a little lime juice, which is added as the milk flows from the vine.

NIPA SALT.—A salt obtained by the burning of the plant known as the *Nipa fruticans*. It is used in the coagulation of Borneo rubber.

MACHACON JUICE.—Cartagena rubber, which is gathered carelessly, is coagulated in a hole in the ground by the addition of the juice of the foot of the “machacon”—a strongly alkaline solution.

POZELINA.—A preparation intended to keep rubber latex in a fluid condition until the time of curing. The ingredients used in making the preparation are secret. The headquarters for its sale are at Para, Brazil.

PURUB.—Another name for hydrofluoric acid, when prepared as a coagulant of rubber latex.

SALT.—Many kinds of low-grade rubber are coagulated by the addition of salt or brine. Borneo, for instance, is coagulated in that way. Madagascar rubber receives a treatment of salt-water. Mangabeira rubber is treated with a mixture consisting of 1 part of salt to 2 parts of alum. Nicaragua rubber is also often coagulated with salt.

SERINGUINA.—A chemical product for retarding for any length of time the coagulation of rubber latex. Is said to contain no corrosive elements. When the latex is finally smoked the substance evaporates entirely. It is the invention of Dr. Cerqueira Pinto, of Para, Brazil.



SOAP AND WOOD ASHES.—The medium-grade rubbers all through Central America are often coagulated by the use of soap, and where that is not plenty, of a strong lye from wood-ashes.

SPIRITS OF WINE.—This is used sometimes in the coagulation of balata.

SULPHUR FUMES.—According to James Collins, rubber of the Para varieties is sometimes exposed to the action of the fumes of melted sulphur, which affects coagulation. This process, however, is very rarely followed.

TORRES SYSTEM.—In addition to the natural methods described above, there are several that give some evidence of an intelligent study of the milk and the substances best adapted for this work. Under the Torres system a liquid is made by a secret formula, from the roots and fruits of certain South American palms, which, when added to the milk, preserves it from curdling, so that it will keep for weeks. It can thus be transported to a convenient place for smoking.

#### COAGULATING MACHINES.

BETA SEPARATOR.—The invention of Mr. John Hinchley Hart, F.L.S., of Trinidad. This is an arrangement by which the latex placed in the upper compartment is washed, filtered, and coagulated. The machine known as the Beta separator works somewhat on the principle of the cream separator.

COUTINHO'S MACHINE.—This is a wooden cylinder about 20 inches in diameter, set horizontally, revolving by a crank and so arranged that smoke is let into the inside through the cylinder shaft. The latex, by the revolution of the cylinder, is distributed over its inner surface and there smoked and coagulated.

DANIN'S machine for smoking rubber is a revolvable cylinder, through openings in the end of which smoke is forced, the latex first having been introduced through the other end of the cylinder. The cylinder being rotated, the latex spreads itself over its inner circumference and is carried past the discharge end of the smoke conduit and thus coagulated. The machine is the invention of J. R. C. Danin, of Para, Brazil.



FUMERO.—A machine patented by G. van den Kerckhove, of Brussels, Belgium. The apparatus is simple, the latex being guided by the hand over the smoke and the rubber produced in ball form uniformly cured. The apparatus designs to do scientifically exactly what the Amazon rubber gatherers do crudely in smoking Para rubber.

FRANK-MARCKWALD PROCESS.—This process is based on the simultaneous employment of dilution and heat, in conjunction with suitable chemicals. It is founded on the injection of latex in a thin jet into a much larger quantity of boiling water. The separated portions almost immediately thrown off are taken out of the water, rinsed, and drawn through rolls to remove the contained water preparatory to drying.

Suitable acids are recommended for various kinds of rubber (such as citric and hydrofluoric); formalin is specially recommended in connection with *Funtumia*. These acids are previously added to the diluted latex. The active principle in this process is the rapid and intense solidification, while the albumen is at the same time separated.

In Dr. Frank's opinion, this process is the most satisfactory yet invented for *Funtumia* and *Ficus*, as well as, so far as experience goes, for *Manihot* latex. The latter coagulated in East Africa on a different system, has not produced satisfactory qualities of rubber.

DA COSTA'S SMOKING AND COAGULATING APPARATUS.—Smoke containing a small amount of acetic acid and creosote is obtained by a wood fire in the furnace of the apparatus, from green palm leaves, nuts, etc. These fumes are held in a special receiver from which they are forced by a steam injector into the coagulating tank. The latex is thus thoroughly agitated and mixed with the smoke. The completely coagulated rubber can be removed in a short time.

WICKHAM'S MACHINE consists of a horizontally revolving cylinder adapted to hold the rubber latex and expose it in a thin layer to the action of smoke which is directed against it. The smoke is produced in a furnace by burning the oily nuts of palms with charcoal and is injected into the coagulating cylinder at a point sufficiently above the level of the latex in

the cylinder to enable each fresh film to form evenly before it arrives in front of the smoke jet. Other suitable agents may be used in place of smoke.

**ELECTRIC COAGULATION.**—Coagulation of rubber latex by electricity has been successfully performed on plantations where acetic acid was scarce. This coagulation is effected in a porous vessel with carbon electrodes, using a low tension current. The latex is slightly diluted with water and the gum separates very rapidly. It is perfectly clear and limpid.

#### CAUSE OF COLOR IN CRUDE RUBBER

The darkening of smoked Para has been demonstrated to be caused by an oxydase or oxidizing enzyme present in the latex and its action on certain oxidizable substances naturally present in the latex, but which may be added to by the smoke.

Dr. David Spence has made some very profound and practical researches on the matter of the darkening of rubber on exposure to the air and his description of the enzymes causing this effect is here appended:

“These enzymes are probably, as I learned, present in the protein of the latex of all rubber-producing plants, and so act upon the insoluble portion of the protein that it is converted into colored products, which impart the dark color to the rubber. In my original work I determined that the temperature at which the oxidizing enzymes are destroyed lies very close to the point where in general other similar enzymes perish. To obtain rubber only slightly darkened, it seems, at first glance, only necessary to destroy the active enzymes in the latex or the rubber by heating above the sterilizing temperature, 75 degrees C. But this method of destroying the enzymes by means of heat is not so easily accomplished in practice, and this fact leads me to the belief that in the latex and in the rubber there was a heat-resisting agent, zymogen, which slowly changed into active enzymes.

“I found, for example, that freshly cut pieces of Para rubber, washed thoroughly with water for more than an hour to remove the strongly colored soluble matters, gradually darkened and after exposure to the air finally became entirely black.

Potassium cyanide, a mercury chloride solution or acetic acid, failed to prevent the dark coloration, or at least after the above solutions were completely removed by washing. I made many experiments with the latex of *Funtumia elastica*, but found without exception that heating the latex of the rubber prepared therefrom even to 100 degrees C. for half an hour was insufficient to alter the tendency to turn dark.

"It is known that certain natives on the West African coast obtain rubber from the latex of *Funtumia elastica* by heating it with water until the separating rubber particles coalesce into balls. Nevertheless, I have seen no sort of rubber prepared in this manner in which the effect of the active oxydase enzyme was not plainly observable.

"Since the oxidizing enzyme is very stable towards heat, the best method for handling the latex to secure only faintly colored rubber appears to be the one presented previously by me and now repeated here. By this method the enzyme itself is to be removed as completely as possible before coagulation. The latex is diluted with water before the coagulation and the agglomerating rubber particles washed well (this applies at least to *Funtumia elastica*) in order to remove the oxidizing enzyme as well as other foreign matter from the rubber. In this manner a snow-white rubber is obtained. Yet to prevent as much as possible the baneful effects when using the boiling process a substance having a noxious action against the enzyme but a harmless one towards rubber could be utilized."

Subsequent to these observations of Dr. Spence, the researches on this problem by Beadle and Stevens resulted in the discovery that the addition of one part of sodium bisulphite to 500 to 1,000 parts of latex neutralizes this enzyme with the result of producing a permanently very pale rubber. This treatment is without injury to the rubber quality and is particularly adapted to white and transparent goods.

It should be remarked that color is not an indication of quality; also the defects of appearance arising from various causes and known as oversmoking, have nothing to do with quality, and the same is true of the appearance of small bubbles in the sheet.

## CHAPTER IV.

### VULCANIZING PROCESSES AND INGREDIENTS— PLANTATION HEVEA AND THE OPTIMUM CURE.

THE means for vulcanizing india rubber in general use are roughly two: the heat cure and the cold cure. Considering the first, a great variety of goods is cured in open steam heat and is kept in shape during vulcanization, either in molds or by being wound with strips of cloth or buried in pans of French talc. This is the wet heat and such goods are cured in vulcanizers, big and little, of which there are many forms. A different application of heat is what is known as dry heat, where goods are put in a hot room without wrapping or mold protection, and left until vulcanization is effected. Another heat cure which at one time was very largely used, but to-day has practically disappeared, was what was known as solarization. This consisted in exposing fabrics coated with a thin skim of rubber to the rays of the sun, which effected a surface cure.

A special heat cure adapted to very particular work, such as curing pure rubber thread sheet, is the water cure. In this method the rubber receives the vulcanizing heat by immersion in water raised to the required degree.

What is known as the cold cure has been practiced since the days of Goodyear, and within the last few years has been much resorted to in the manufacture of certain lines of goods. This in turn, divides itself into two methods—the acid and the vapor cure. In the former, one-half pound of chloride of sulphur is mixed with four pounds of bisulphide of carbon. The goods are dipped in this solution and afterwards treated with an alkaline wash. The vapor cure is where the fumes of chloride of sulphur are set free in a heated room or cabinet in which the rubber goods are suspended so that all of the surface is affected. When the cure is far enough advanced the

further action of the chloride of sulphur fumes is stopped by ammonia fumes.

While Charles Goodyear's patents for the vulcanization of india rubber by the use of sulphur and heat were in force, a marvelous amount of ingenuity was shown in the attempts to accomplish the same results by the substitution of other ingredients for sulphur, either with or without the use of heat. These experiments and inventions embrace vulcanization, by means of chlorides, nitrates, nitrites, fluorides, bromides, iodides, and phosphorets of about all the common earths and metals, and also many gases such as sulphurous acid gas. The majority of these experiments have been lost sight of, partly because the Goodyear process is now open to the world, and partly because, for the majority of goods, the sulphur and heat cure is not only the cheapest, but the easiest to accomplish. It may be well, however, to review and record the experiments in this line, as there is no doubt that for special lines in rubber manufacture many of them have a suggestive value today.

One of the very first ingredients to which inventors and experimenters turned their attention was zinc. The veteran rubber manufacturer, Jonathan Trotter, described a process for preparing a vulcanizing material which he called hyposulphite of zinc. It was made from a solution of caustic potash saturated with flowers of sulphur and then treated with sulphurous acid gas. This solution he mixed with a saturated solution of nitrate of zinc, forming the precipitate that he desired. He used 3 pounds of hyposulphite to 10 pounds of rubber, curing from 3 to 5 hours, at 260 degrees to 280 degrees F.

E. E. Marcy, an American, some years later patented a compound of hyposulphite of zinc and rubber which is apparently almost identical with Trotter's discovery, although he disclaimed similarity, and also made public the process, in which he used a combination of hyposulphite of zinc and sulphide of zinc, the compound being 2 pounds of rubber, 1 pound sulphide of zinc, 1 pound hyposulphite of zinc, and other ingredients as deemed necessary. These goods were of a beautiful white color, were said not to bloom, and did not need the sunning process then in use. At the same time they depended upon sulphur and heat for whatever vulcanizing was accomplished.



Another attempt to get a good substitute for sulphur was in the production of what is known as sulphite or hyposulphite of lead. James Thomas describes at length a compound in which he mixes hyposulphite of lead and artificial sulphide of lead in equal proportions, his compound being for vulcanization, 2 parts by weight of india rubber and 1 part of the vulcanizing material.

Following this thought came E. E. Marcy again, who mixed sulphide of lead and carbonate of lead in the proportions of 2 parts of sulphide of lead, 1 part carbonate of lead, and 2 parts protoxide of lead in place of the carbonate.

Then Oscar Falke and Albert C. Richards brought out a compound consisting of 6 parts india rubber, 2 parts sulphide of antimony, and  $\frac{1}{2}$  part sulphite of soda, curing at 270 degrees to 280 degrees F.

A. K. Eaton, in no uncertain terms, disclaimed vulcanization by the use of free sulphur, but claimed to be the first to use sulphide of manganese. He also gave a formula for making it, which was by mixing intimately 44 parts of peroxide of manganese with 32 parts of sulphur, and exposing the mixture to heat in a covered crucible. He vulcanized several hours, from 250 degrees to 310 degrees F.

George Dieffenbach claimed sulphite of alumina as an ingredient which, in connection with heat, would bring about vulcanization. He used this in a compound for a dental rubber, which had for its basis india rubber, amber, linseed oil, sulphide of cadmium, oxide of tin, vermilion, and pulverized feldspar.

Charles T. Harris cured india rubber by combining it with an artificial sulphide of bismuth, which he explained as being the artificial tersulphide, or polysulphide of bismuth. He describes this as being a heavy black powder, and the compound which he advised for soft rubber was 100 parts india rubber, 75 parts carbonate of lead, and  $12\frac{1}{2}$  parts polysulphide of bismuth, cured in a dry heat at 245 degrees F. for  $1\frac{1}{2}$  hours.

Henry W. Joselyn discovered that shale combined by heat with sulphur formed a sulphide which could be used in curing rubber, and hastened to patent it.



Andreas Willman brought out a process for combining india rubber with "anhydrous chlorides, sulphates of alkalies" and powdered coke or coal, and claimed that his best result came from chloride of ammonium and coke. His compound was made up of litharge, lampblack, and powdered coke, in connection with from 2 to 10 per cent. of his vulcanizing mixture.

Edwin L. Simpson formed a vulcanizing compound by mixing benzoin gum with pulverized sulphur, and boiling it in linseed oil. It was used in a dry heat, the compound being 1 pound of india rubber, 2 ounces vulcanizing compound, 8 ounces litharge, and 8 ounces whiting.

J. A. Newbrough manufactured a vulcanizing material which he called acid resin, made of turpentine and sulphuric acid. This he incorporated in india rubber in the proportion of 6 ounces of acid resin to 1 pound of india rubber, and cured at 300 degrees to 320 degrees F.

The use of selenium as a curing agent was discovered by E. E. Marcy, while connected with Horace H. Day, then prominent as a rubber manufacturer. He advised the use of equal parts of india rubber and powdered selenium, and, to produce a glossy finish, he added selenium carbonate and whiting.

At the same time there were many other inventors who were experimenting with processes that were somewhat in the line of the well-known Parkes cold-curing process. For example, it is a matter of history that the late Joseph Banigan, early in his career as a rubber manufacturer, cured wringer rolls by an acid process.

Dubois C. Parmelee invented a process which he called "hermizing," to distinguish it from curing or vulcanizing, instead of the Parkes process, in which the solution of chloride of sulphur and bisulphide of carbon was used. He recommended briefly a solution as follows: 10 pounds of coal-tar naphtha, in which was dissolved 1 pound of sulphur. Into this solution he passed dry chlorine gas until it assumed a fine yellowish-green color. This solution he used as a dip for such goods as would be cured by the acid treatment. Parmelee also claimed the discovery of a solution made of coal-tar naphtha,

bisulphide of carbon, and a solution of sulphur in bromine, mixed with this.

R. F. H. Havermann reduced india rubber to a solution and subjected it to the action of chlorine. He also, in a later patent, described the washing of the chlorine out of the rubber by alcohol, and the addition of ammonia and lime, the result being, according to his specifications, a white, hard rubber.

Working in the same line, John Helm, Jr., dissolved india rubber in benzine and mixed it with liquid chlorine in the proportion of 12 ounces of chlorine to 1 pound of gum. His claim was that he could get rubber of any color and of any degree of hardness by this process.

H. A. Ayling patented a cold-curing process in which carbon spirits (naphtha), one of the petroleum series, was mixed with chloride of sulphur, instead of the usual bisulphide of carbon.

In the line of hard rubber manipulation and vulcanization, L. Otto P. Meyer (then connected with the India Rubber Comb Co.) patented a process for curing vulcanite in a vessel wholly or partly filled with water, the water in which the rubber was contained being in a tight receptacle, and the heat being raised above 300 degrees F., the pressure of the surrounding steam keeping it from vulcanizing. This obviated the danger of burning, and was of great value in the production of certain goods.

While these and other inventors were trying to cure rubber without sulphur, and without interference with the Good-year patents, certain others were at work on other gums. For example, John Rider, who was at the head of a gutta-percha company, produced what he called mettaloethyanized gutta-percha. In this, he first heated the gutta-percha, then mixed 3 pounds of hyposulphite of lead and zinc with 8 pounds of gum, and sometimes added also a little Paris white, or magnesia. He then put the compound from 2 to 10 hours in a dry heat and cured it at 280 degrees to 320 degrees F.

John Murphy changed this compound somewhat, by advising the incorporation of sulphur in the proportion of 2 to 6 ounces of sulphur to 10 pounds of gutta-percha. This sulphur, by the way, obviated the preliminary heating of the gutta-percha,

which was supposed to volatilize the ingredients that had before rendered it unvulcanizable.

William Mullee brought out a curious process for the manufacture of hard rubber. In this, just as soon as the rubber was washed, the sheets were immersed in the sulphur bath, heated to 220 degrees F. The water and other impurities in the rubber were said to be extracted by the action of the heated sulphur. After boiling 30 minutes, the sheets were removed and washed to prevent crystallization. They were then subjected to the same process a second time. The rubber was then compounded in the usual way, on rolls, the proportions being 17 to 24 ounces of sulphur to 16 ounces of rubber. The claim for this was that the compound when cured was tougher than any others ever known.

William Elmer prepared what he called "elastic selenide of caoutchouc." He first dissolved the india rubber in bisulphide of carbon, placed it under pressure, and heated gradually. When brought to about 300 degrees F., the liquefied selenium was put into the apparatus drop by drop, the solution in the meantime being kept in constant motion. This elastic selenide he claimed to be semi-fluid which, when evaporated, possessed all the characteristics of india rubber.

The Parkes cold-curing process is so widely known as to require but a word. It is based on the invention of Alexander Parkes, and depends upon the faculty that chloride of sulphur has for vulcanizing india rubber. Chloride of sulphur may be applied for vulcanization either as liquid or as vapor.

A great many thin sheet rubber goods are cured by the vapor process. This is done in many cases by hanging the goods in an air-tight chamber, like a dry heater, and passing the vapor, which is either that of chloride of sulphur alone, or chloride of sulphur mixed with carbon bisulphide, into the curing room. Small articles are often put in a tumbling barrel made of wire, which revolves slowly in the vulcanizing room, thus giving the vapor a chance to do its work thoroughly. The rubber surfaces are of course dusted first, to keep them from adhering. Proof cloth is cured in vapor by passing the rubber surface over troughs in which this reagent is slowly evaporating.

Parkes also suspended articles to be vulcanized in a dry heater and passed the following gases into the chamber as a means of vulcanization: Sulphurous acid, gas, chlorine, nitrous acid, or the vapors of bromine or iodine.

Charles Hancock cured rubber by the action of vapors produced by dissolving zinc, copper, or mercury in nitric acid. The action of these vapors being so active, only one or two moments were given, and the surfaces then washed in an alkaline solution.

Nickels passed sulphur fumes and hydrogen into the gum while in a masticator, curing afterward by heat.

Caulbry's process is similar to that of Parkes's, by which it is claimed rubber can be vulcanized at ordinary temperatures, by using an intimate mixture of chloride of sulphur and dry chloride of lime. During this mixture, and when the smell of the chloride of sulphur will be noticed, the temperature of the mixture will rise, the mass becoming plastic by the softening of the sulphur. If a mixture of this kind, in which sulphur is in great excess, be added to the solution of india rubber in bisulphide of carbon, the rubber will be vulcanized at an ordinary temperature, or perhaps with a slight warming. Chloride of sulphur used pure is too corrosive in its effect on india rubber; it is therefore reduced in all cases. Only thin articles can be vulcanized in this way.

A patent taken out in England by Edmond Garnier relates to the vulcanization of india rubber by the use of alum. Previously alum processes for curing had not been very successful, but this patent had some novel features. It called for particularly dry alum treated with a solution of terebinth of benzol and shellac, or some similar gum. In use he took 8 ounces of alum and a solution composed of 1 part gum and 20 parts benzol. He mixed the ingredients that are usually employed in the manufacture of rubber, specifying 3 pounds of whiting, 1 pound barytes, 8 ounces lime,  $1\frac{1}{2}$  pounds oxidized oil, and 8 ounces of india rubber. When these had been thoroughly mixed together and specially treated, alum was incorporated with them and well compounded, being passed through the mixing rollers cold. It was then calendered.

Raymond, in another English patent, uses for vulcanizing a mixture of benzine, camphor, chloride of sulphur, and oleic acid.

#### VULCANIZATION BY ULTRA-VIOLET RAYS.

VULCANIZATION by ultra-violet rays was brought to the attention of the rubber industry by Dr. Helbronner and Dr. Bernstein, at the International Rubber Conference at London in 1914. It is said that Victor Henri in 1909-1910 was the first to expose rubber to the ultra-violet rays, carrying out vulcanization with films of solution. French patent No. 460,780, issued July 26, 1913, international conventions, date July 26, 1912, claimed the vulcanization of rubber solutions by ultra-violet rays and states that 3 per cent. plantation rubber and sulphur in benzine exposed in thin layers vulcanize rapidly, sulphur to the extent of from  $1\frac{1}{2}$  to  $2\frac{1}{2}$  per cent. combining with the rubber.

Crystalline sulphur, rather than flowers of sulphur or stick sulphur, should be used and the interesting suggestion is made that these solutions of rubber so vulcanized may have industrial application. They are said to be suitable for all kinds of cementing or rubberizing operations, and are capable of resisting all mechanical strains, as well as the action of heat. They can be used particularly for joining and rubberizing leather, and consequently will be valuable in the shoe industry.

Also, the repairs of all rubber goods, tires, inner tubes, etc., can be readily carried out by means of vulcanized solutions.

Two other patented methods of vulcanization by ultra-violet rays may be mentioned.

#### OLIVIER'S METHOD.

THE rubber solution, containing free sulphur, with or without certain organic or inorganic sulphides which are decomposed by ultra-violet rays, such as carbon bisulphide, allyl sulphide, or antimony sulphide, passes from a hopper on to an endless steel band, which is carried by guide rollers round the greater part of the periphery of a mercury-vapor lamp. The lamp is surrounded by a double, hemicylindrical water-jacket of quartz,



in order to cut off heat rays. The time of exposure is quite short, in order to avoid the deleterious effect of prolonged exposure to ultra-violet radiation on the rubber. As an example, a layer of solution a fraction of a millimeter thick, at a distance of 5 centimeters from the lamp, which is operated at 220 volts and 3 amperes, requires an exposure of about 40 seconds. After passing the lamp the solution is removed from the endless band to a receiving vessel by means of a scraper.

#### BERNSTEIN'S METHOD.

THIS consists in the exposure of rubber solution containing sulphur, sulphide, or other vulcanizing agents to the action of ultra-violet rays under conditions to suit the circumstances, such as *in vacuo*, under heat and pressure, or in an atmosphere of neutral gas not containing oxygen.

Helbronner and Bernstein consider vulcanization as a mere polymerization of the rubber under the action of a catalytic agent (sulphur). The sulphur becomes insoluble and unites with the india rubber. A certain action of the rubber is caused by the ultra-violet rays, and another by the sulphur, and the combined actions produce vulcanization. The sulphur becomes the catalyser under the action of the ultra-violet light.

#### PRESSURE CURE.

PRESSURE cure is the designation covering the several patented methods of vulcanization by heat and sulphur, conducted either in air or an inert gas under pressure. It is one of the recent improvements in rubber shoe manufacture, displacing the ordinary steam-heated dry-air vulcanizing method, particularly for boots and heavy goods. The method originated in the United States. The chief advantage of pressure cure for rubber footwear seems to be greater solidity of the rubber composition and more perfect contact of adjacent parts in the structure of the goods due to expulsion of air by pressure. Essentially this result is also attained by subjecting the goods to vacuum or pressure treatment previous to the ordinary dry-heat curing without pressure.

#### ELECTRIC VULCANIZATION.

THE substitution of electricity for steam is not new, but an improved method of vulcanizing rubber by electricity has



recently been patented that, according to the claims, not only effects a great saving in heat and labor, but insures a more uniform cure in less time. Metal contacting strips or plates are employed, through which is passed an electrical current, that is maintained for the proper length of time to effect a cure. By constructing the heating strip or plate at different points with sections of varying electrical resistance, the vulcanization of belting, packing, mats, tires and molded goods may be accomplished.

#### SULPHUR BATH VULCANIZATION.

VULCANIZATION by immersion in a bath of molten sulphur is adapted for the cure of pure rubber "dipped" articles or those made of cut sheet. It is conducted, at temperatures varying from 135 to 160 degrees Centigrade, in a specially constructed apparatus in which the melting of the sulphur is effected by a direct firing plant. The sulphur vapors are removed by a powerful exhauster. The vulcanized articles are freed from adhering sulphur by heating in soda solution.

#### VULCANIZING INGREDIENTS.

AMORPHOUS SULPHUR.—The fusion of 1 pound of sulphur with 4 ounces of Canada balsam produces what is known as amorphous sulphur, which is said to cure rubber so that it will have no tendency to bloom. The preparation has a very pungent sulphurous odor. Patented by Dr. Wilhoft, of New York.

ARTIFICIAL SULPHURET OF LEAD.—There are several combinations of lead and sulphur which may be produced artificially. That one containing the most sulphur has a composition of 13 per cent. of sulphur and 86 per cent. of lead. Its specific gravity is about 9.4. In color it is black. The other sulphur compounds of lead have much less sulphur, one containing but 9 per cent. and the other only 4 per cent. What is known as hyposulphite of lead is a mechanical mixture of the above first named, with a suitable percentage of sulphur to effect vulcanization. It is also known in the rubber trade as "Eureka compound," "burnt hypo," and "black hypo." These compounds when pure—that is, when free from adulteration—are of great value. They produce goods that are jet black and

have little odor and are free from bloom. They are reckoned as the safest vulcanizing agents, as it is almost impossible to burn goods that depend upon their presence for cure. They are used in either dry or wet heats.

**BARIUM SULPHIDE** is prepared from heavy spar by making a dough of it with charcoal and oil and subjecting it to a white heat. Sulphides of the alkaline metals, potassium, sodium, calcium, and barium, will vulcanize rubber, whence the term "alkalized rubber."

**BROMINE**.—A heavy deep red volatile liquid, possessing a most peculiar and unpleasant odor, and giving off vapors most irritating to the air passages and lungs. Its very name means stench. It has a powerful action upon most organic bodies, coloring animal matter brown, while it bleaches coloring matters, dyes, etc. Its specific gravity is 3.18. A piece of sheet rubber dipped into bromine is vulcanized instantly. It is somewhat soluble in alcohol, and very soluble in ether, bisulphide of carbon, chloroform, etc. Newbrough and Fagan filed two patents in the United States for the use of bromine in vulcanization, both with and without iodine. By adding to iodine  $\frac{1}{2}$  its weight of bromine, proto-bromide of iodine is formed, which is said to combine with india rubber and produce a hard compound on being exposed 1 hour to a temperature of 250 degrees F. To prevent the forming of an explosive the iodine and bromine were separately treated with oil of turpentine to which had been added a quarter of its weight of sulphuric acid. It was then mixed with the gum in the proportion of 2 pounds 11 ounces to every pound of gum. Bromine was also used alone by these inventors, the material after molding being plunged into the liquid, and left there long enough to harden. To prevent the hardening of the material while in the bath, chloroform or any other solvent of rubber was added in the proportion of 1 part to 9 parts of bromine; in other words, the rubber vulcanized in the air after its withdrawal from the liquid.

**CHLORINE**.—Chlorine is a greenish yellow gas at all ordinary temperatures. It has strong bleaching properties and also a very bad smell and action upon the respiratory passages. Under a pressure of 127 pounds to the square inch at 60 de-

grees F., chlorine condenses to a yellow liquid, having the specific gravity of 1.33. Chlorine cannot, as a rule, destroy mineral colors or blacks produced by carbon. Helm claimed that he was able to produce white hard rubber by incorporating chlorine with the mass.

CHLORIDE OF SULPHUR.—Sulphur and chlorine form three compounds, the monochloride, the dichloride, and tetrachloride of sulphur. The substance commonly used in the arts is the first named or a mixture of the first two. It is an oily liquid of the specific gravity 1.7 and boiling at 239 degrees F. It has a pungent smell and decomposes on contact with water or watery vapor. Pure chloride of sulphur is of an orange yellow color of great density. It fumes strongly when exposed to the air, throws off the vapors of hydrochlorine, and is quite poisonous, severely attacking the mucous membranes. It is widely known as the active agent in Parkes's cold-curing process, where it is used in connection with bisulphide of carbon. A common formula for this is chloride of sulphur, 1 part by weight, bisulphide of carbon, 30 to 40 parts by weight; immerse from 60 to 80 seconds. In the manufacture of balloons and toy balls, the solution is a far weaker one. That for the outside dip is 10 parts of chloride of sulphur to 100 parts bisulphide of carbon, while for the inside it is 16 parts chloride of sulphur to 100 parts bisulphide of carbon. When it was common to cure proofed cloth by the cold process, it was done by wetting its surface with a mixture of 5 to 10 parts of chloride of sulphur, dissolved in 100 parts of bisulphide of carbon, then running the fabric over heated drums to evaporate the mixture. In the sulphurization of oils for rubber substitutes chloride of sulphur plays a most important part, nearly all of the amber and white products being produced by its use. It also has a curious effect upon bastard gums, giving some of them temporarily the elasticity and appearance of high-grade rubber.

GOLDEN SULPHURET OF ANTIMONY.—This is prepared from black antimony by boiling it with caustic soda and sulphur for some time. The liquid is then clarified by filtration or settling and the clear part treated with a dilute acid, preferably muriatic or sulphuric. A golden yellow precipitate is formed which

should be well washed in water, and dried at not too high a temperature in a darkish place. The results of this operation well carried out are constant and the composition should be: Antimony, 60.4; sulphur, 39.6. Golden sulphuret of antimony heated in a tube will give off sulphur which will deposit on the cool sides of the tube away from the flame and the residue will turn black, being indeed the black sulphide of antimony. All samples of this compound should be tested for free acid, by shaking up a little of the powder in a test tube with cold or hot water, and testing the water afterwards with some barium chloride and blue litmus paper. A white cloud in the first place and the reddening of the paper in the second place indicate the presence of more or less free sulphuric acid. Golden sulphuret prepared with muriatic acid will not respond to the first test, but will to the second.

Golden sulphuret or antimony red (pentasulphide) is used more largely than any other form of antimony in rubber work. It is also called orange sulphide of antimony.

Its composition is pentasulphide of antimony with calcium sulphate carrying free colloidal sulphur. The following typical analysis represents a standard American grade:

Antimony, as pentasulphide .....	30.00
Calcium sulphate .....	43.00
Free sulphur .....	17.00
Water of crystallization .....	9.00
Moisture .....	1.00

The calcium sulphate and water of crystallization are present as legitimate constituents and are in no sense adulterants.

Golden antimony may be made with various percentages of free sulphur, although the usual standard is 17 per cent. for rubber work. As ordinarily used this allows ample sulphur for vulcanization.

Properly used, this ingredient produces some of the best effects found in vulcanized rubber, in color, texture, and durability. It should never be mixed on a very hot mill, should be sheeted and placed in cooling racks if it is not to go right to the calender, and should be cured in as low a heat as possible. The ideal result will be of a golden yellow color, with a very slight bloom, if any. It is used only in high cost goods.

In rubber compounding golden antimony serves several important purposes. It is valuable as a pigment but, aside from this, its function is chiefly chemical, since it furnishes sulphur in colloidal form for curing. This is ideal for vulcanization, because the rubber can be fully cured without containing an excess of sulphur to cause unsightly blooming and subsequent deterioration by aging. The use of antimony also results in producing tough stock of increased tensile strength over pure rubber and sulphur as found, for example, in automobile tubes and rubber bands.

**HONEYCOMB SULPHUR.**—A vulcanizing compound made by boiling a pound of sulphur and two ounces of benzoin gum together, 1 pound of this material being mixed with a quart of boiled linseed oil.

**HYPOSULPHITE OF LEAD.**—See Artificial Sulphuret of Lead.

**IODINE** is manufactured from seaweed and is a black-gray substance occurring in small shining scales. Its specific gravity is 4.94 and it fuses at 239 degrees F., giving off violet vapors. It is readily soluble in alcohol, benzol, chloroform, and sulphide of carbon. In addition to the formula given under the head of bromine, Newbrough and Fagan patented the combination of iodine and sulphur. In this the sulphur was boiled in turpentine, and the oil decomposed and deposited with the sulphur at the bottom of the vessel was used in the operation, after being washed in dilute sulphuric acid and dried. The iodine was treated in the same manner to prevent explosions. Equal parts of each were melted together and incorporated in the proportion of 2 ounces 5 drams to 1 pound of rubber. After shaping, the articles were put in a vulcanizer and during the first fifteen minutes exposed to a dry heat, gradually increasing to 320 degrees F., remaining there 5 minutes, then dropping rapidly to 250 degrees F., and continuing for an hour at that temperature.

**LIVER OF SULPHUR.**—This is really pentasulphide of potassium, and is obtained by mixing carbonate of potassium together with sulphur. It is called liver of sulphur on account of its brown color. As it is quite volatile it should be kept in



well closed glass vessels. The fluid for vulcanizing purposes is a concentrated solution of the pentasulphide, about 25 degrees Baumé being right for use. To cure with it the liquid is brought to the boiling point in a porcelain vessel, the articles to be vulcanized being immersed in it. This is known as Gerard's process and is said to be inexpensive and perfectly safe.

MILK OF SULPHUR.—In America this material and precipitated sulphur are identical and officially 99.5 per cent. pure. In Great Britain, milk of sulphur contains approximately 50 per cent. of calcium sulphate, while precipitated sulphur is officially 99.5 per cent. pure and is the form utilized in rubber work.

NANTUSI is a vulcanizing agent and preservative for rubber, consisting of sulphur and paraffin, and in use in England. It is offered as preventing the superficial cracking of rubber exposed to the atmosphere; preserving the quality of the rubber; doing away with the possibility of acidification in sulphur as ordinarily used; and reducing the cost of the mixing. It is said to be a special mixture of paraffin and sulphur.

PENTASULPHIDE OF ANTIMONY.—The chemical name for golden sulphuret of antimony (which see).

PROTO-CHLORIDE OF SULPHUR.—See Chloride of Sulphur.

SULPHIDE OF LEAD.—Occurs native as galena and is one of the ores of lead, having a specific gravity of 7.2 to 7.7. Commercially it is a black powder, of specific gravity 6.9. Its composition is 86.6 per cent. of lead and 36.4 per cent. of sulphur. Sulphide of lead is a very useful black pigment, and one that is used quite largely in rubber works, as it is a good filler and assists in vulcanization. It is often made from pure white lead by very simple treatment. It materially assists the resiliency of Para compounds.

SULPHUR LOTUM.—A name for sublimed sulphur that has been washed to remove sulphurous acids, and carefully dried.

SULPHIDE OF ZINC.—Sulphur forms with zinc two sulphides. One of these, the monosulphide, corresponds to zinc



blende, which, as found native, is of various colors, from yellow to black. Its specific gravity is from 3.5 to 4.2. The other is a pentasulphide artificially prepared and occurs in the form of a white powder. Upon ignition in the absence of air this latter substance loses four-fifths of its sulphur but the temperature at which this takes place is too high to render it available as a source of sulphur of vulcanization in compounding rubber mixtures. With a slight addition of sulphur it is used in the production of white goods.

SULPHUR occurs in a number of different forms, and under various names as brimstone, flowers or flour of sulphur, roll sulphur, rock sulphur, etc. Its specific gravity is 1.98 to 2.06. It melts at 239 degrees F., thickens and becomes orange yellow at 320 degrees F.; at 428 degrees it is semi-solid and red, and on carrying the heat higher it becomes browner and boils at 788 degrees F. Some of the sulphur now used commercially is recovered from alkali waste; formerly most of it came from Sicily, where it is found native. The American supply now comes largely from Louisiana, where, by the injection of steam to deep-lying deposits, the sulphur is melted and forced to the surface. It is more generally used in rubber works than any other ingredient, and in all proportions from 3 per cent. up to 100 per cent. of the weight of the rubber. The ordinary form in which it is found in the rubber factory is in a yellow powder, known as flowers of sulphur. It has a slight affinity for moisture, and careful manufacturers keep it covered from air to avoid the formation of sulphurous or sulphuric acids. Combined with certain oils by heat, it forms the black sulphur substitutes that are often used in rubber compounding. Sulphur in the form of rolled brimstone is pulverized, sifted and used in the place of flowers of sulphur, in France, and is equally good and cheaper.

SULPHUR BALSAM.—A solution of sulphur in fixed oils, consisting of 2 ounces of flowers of sulphur in 8 ounces of linseed oil, used in proofing compounds.

VESUVIAN WHITE.—A special vulcanizing material manufactured in England, for use in the manufacture of tennis balls and other goods.

**VULCANINE.**—An English vulcanizing preparation, used for both steam and dry heat goods. It occurs either as a white or a black powder, depending upon the line of goods on which it is to be used.

**VULCOLE.**—A paste furnished in two colors, white and black, added to certain compounds, prevents blooming. It also has the quality of rendering flowers of sulphur inert if used in excess, so that 50 to 75 per cent. can be used in an ordinary soft compound.

The table following indicates vulcanizing pressure in pounds per square inch in gage, and corresponding temperatures by the Fahrenheit scale:

VULCANIZING PRESSURES AND TEMPERATURES.

Pressure in lbs. per sq. inch in gage.	Tempera- ture in Fahren- heit degrees.	Pressure in lbs. per sq. inch in gage.	Tempera- ture in Fahren- heit degrees.	Pressure in lbs. per sq. inch in gage.	Tempera- ture in Fahren- heit degrees.
7	232.3	39	285.4	71	316.7
8	234.7	40	286.6	72	317.5
9	237.1	41	287.8	73	318.3
10	239.4	42	288.9	74	319.1
11	241.6	43	290.1	75	319.9
12	243.7	44	291.2	76	320.7
13	245.8	45	292.3	77	321.4
14	247.8	46	293.4	78	322.2
15	249.7	47	294.4	79	323.0
16	251.6	48	295.5	80	323.8
17	253.5	49	296.5	81	324.5
18	255.3	50	297.5	82	325.2
19	257.0	51	298.6	83	326.0
20	258.7	52	299.6	84	326.7
21	260.4	53	300.6	85	327.4
22	262.0	54	301.5	86	328.1
23	263.6	55	302.5	87	328.9
24	265.2	56	303.5	88	329.6
25	266.7	57	304.4	89	330.3
26	268.2	58	305.3	90	331.0
27	269.7	59	306.3	91	331.7
28	271.1	60	307.2	92	332.3
29	272.6	61	308.1	93	333.0
30	273.9	62	309.0	94	333.7
31	275.3	63	309.9	95	334.4
32	276.7	64	310.8	96	335.1
33	278.0	65	311.6	97	335.7
34	279.3	66	312.5	98	336.4
35	280.5	67	313.3	99	337.0
36	281.8	68	314.2	100	337.7
37	283.0	69	315.0		
38	284.2	70	315.8		

## PLANTATION HEVEA AND THE OPTIMUM CURE.

THE reliability of fine hard Para from wild Amazonian sources serves as a standard for the preparation of plantation fine as they are both derived from *Hevea brasiliensis*. A great deal of scientific research has been devoted to seeking the causes of variation in the time required to vulcanize smoked and un-smoked plantation fine to the optimum cure, by which is meant the best physical results attainable from a given specimen of rubber.

Exhaustive investigations in this field have been carried on continuously for several years in the chemical laboratory and experimental vulcanizing factory of the Department of Agriculture, Federated Malay States, by B. J. Eaton and J. Grantham. The details of this study have been published at intervals in the "Journal of the Society of Chemical Industry," London. It is sufficient here to indicate the results by brief abstracts and quotation of summaries as given by the authors.

There is a marked tendency to look to fine hard Para as the standard because manufacturers have had experience with it extending over many years. That, however, is the only argument in its favor. The term uniformity, as applied to rubber, means rubber of the same type. Different types of rubber may vary in mechanical strength, but variation in vulcanizing quality is far more important to the rubber manufacturer. The matter of form and appearance is of little consequence to the manufacturer, although important to the broker, buying and selling on looks rather than by test.

In vulcanizing rubber with sulphur the manufacturer has recourse to three methods in securing a given result. He may vary the amount of sulphur, or the temperature and time of vulcanization. In the experimental work of the agricultural department, the sulphur and temperature were fixed and the time varied. In the original experiments all the rubbers tested gave their best results in  $2\frac{1}{2}$  to  $2\frac{3}{4}$  hours. Different mechanical results were obtained by changing the time of cure.

Rubber consists approximately of 94 per cent. of caoutchouc, 1 per cent. of mineral salts, 2 to 3 per cent. of resins, and 2 to 3 per cent. of protein. The ingredient most liable to

change is the protein, and probably some substance derived from this acts as an accelerator. Experimentally it was found that this change occurs in the coagulum if left for six days before being crêped. No evidence of this change can be detected in the appearance of the rubber, which in consequence requires to be tested to ascertain its vulcanizing quality.

As concerns rubber estate practice several factors affect vulcanization. These are thickness, *i. e.*, amount of serum removed; smoking, which retards vulcanization; the use of formalin or other preservatives; amount of acetic acid used in coagulation, and the dilution of the latex. The age of the tree also affects the proportion of protein and other constituents of the latex.

The more uniform methods now adopted on many estates tend to greater uniformity of product; but variability is due chiefly to the difference in rubber from different estates.

In these experiments, in preparing the block of pan coagulum, which was left in this form for some days, a really new type of rubber has been discovered. It vulcanizes more rapidly than fine hard Para and ordinary plantation grades, which take medium time. Only eight or nine samples of fine hard Para have been tested so far, but it is remarkable that all vulcanized in about the same time.

It is, therefore, natural for the small manufacturer to rely on fine hard Para. The reason for its lack of variation is attributable to the uniform method of its preparation, and not because of any intrinsic value of the method. As it may require two or three months to prepare a ball of fine hard Para, any variations in its quality are averaged.

The formation of the accelerating substance is believed to be effected by bacteriological action. Rapid-curing samples show better mechanical tests than those that cure slowly.

Rapid vulcanization eliminates the danger of overheating, and that is probably the reason for the increase of strength.

Dr. Schidrowitz first pointed out this variability in rate of cure in plantation rubber, of which the experiments at the agricultural department first showed the cause. It is possible

now to prepare a rubber which will vulcanize correctly at any particular time, within certain limits.

Subsequent experiments have been directed to ascertaining the nature of this accelerating substance and its behavior under different treatments, to determine its probable constitution. These efforts have resulted in the isolation or preparation of a substance or substances from the latex serum to which acceleration in rate of cure can be attributed, and evidence has been obtained of the presence of a second substance which also has a similar effect.

The experimental results confirm the theory that the rate of cure is influenced by the amount of an accelerating agent formed by the decomposition of some constituent of the latex, and that this substance is a decomposition product of the protein or nitrogenous constituents of the latex, produced usually in the freshly coagulated raw rubber by the action of micro-organisms, which gain access to the latex after it leaves the tree, or possibly in some cases decomposition by chemical action. The retarding effect of smoking, on the rate of cure, has proved to be a more complicated problem than at first appeared. The retarding effect, though invariably shown by slab, has been found not to be constant in sheet, especially in thin sheet. This is due to the fact that, in smoking rubber, more than one variable factor, influencing the rate of cure, is present.

In most of their experiments the authors, Eaton and Grant-ham, used raw rubber in the form of slab slightly pressed, or unpressed coagulum containing a large percentage of serum. The latex was coagulated one day about noon, left in the serum till about 10 A. M. the following day and then rolled under a wooden rolling pin on a sloping table. All samples were eventually converted to thin crêpe before vulcanizing.

#### CAUSES OF VARIABILITY IN RATE OF CURE.

The investigation is in three divisions:

##### PART I.—EXPERIMENTAL.

Part I embraces a group of experiments for determining—  
The time necessary to develop the change in slab rubber, causing an increase in rapidity of cure.



The effect of antiseptics, heat and cold.

The effect of formalin.

The effect of soaking in running water.

#### CONCLUSIONS UNDER PART I.

1. That the rate of vulcanization of rubber from any given latex is determined by the extent to which a certain change takes place subsequent to coagulation.

2. This change is normally limited to the first few days after coagulation. The change is progressive and reaches a maximum in "slab" rubber (*i. e.*, coagulum containing a large proportion of the serum) in approximately six days after coagulation.

3. The change can be arrested either partially or completely by the action of formalin, heat, and cold. It is also arrested by crêping shortly after coagulation, which may be due either to the larger surface exposed or to the more rapid drying, or both, combined with the removal of most of the serum in machining to crêpe form.

4. The complete arrest or inhibition of the change by formalin (similar effects have been obtained with other antiseptics) and by the action of both heat and cold, indicates the formation by biological action of a substance which increases the rate of cure of raw rubber, the decomposition being probably of an anaerobic nature. There is no evidence that the change is due to chemical agencies.

In this connection experiments carried out on latex frozen for several days at 12 to 15 degrees F., are of considerable interest, since by freezing for this period, the rubber no longer cures rapidly, even if left for a considerable period afterwards at 84 degrees F.

[The method of freezing latex to produce rubber has been patented in the Federated Malay States. Latex after freezing for 4 to 5 hours is coagulated and, on thawing the solid block thus formed, a solid coagulum is formed, whereas latex can be frozen for a short period and on thawing is reconverted into latex.]



## PART II.—EXPERIMENTAL.

Part II deals with the probable nature of the constituent of the latex involved in the changes in raw rubber, and the nature of the constituents which are responsible for the variations in rate of cure of different rubbers.

The experiments of Part II included the addition of proteins to rubber and the effect was determined of the following additions:

- Casein and peptone.
- Decomposed casein.
- Protein from the latex.
- Evaporated serum minus protein.
- Decomposed protein from serum.

## CONCLUSIONS UNDER PART II.

There exist in serum two substances: (1) a substance of the nature of protein, precipitated or coagulated by heat, which is ineffective in accelerating the rate of vulcanization unless decomposed; (2) a soluble substance, only obtained by evaporation and not easily decomposed, which has itself an accelerating action on vulcanization.

Decomposed precipitated protein is effective in much smaller quantity than serum residue obtained by evaporation, after the heat coagulated protein has been removed.

In the ordinary preparation of sheet and crêpe rubbers the greater part of the serum is removed in machining the coagulum, and the whole of the soluble products may be washed out in crêping, so that normally the accelerating effect of the soluble serum is nothing. All of the experiments of the first part show the gradual development of the accelerating substance during the first few days after coagulation. This is attributed to the decomposition of protein (similar in nature to that precipitated from the serum by heat), which is precipitated with the rubber during coagulation.

## PART III.—ANALYTICAL. NITROGEN CONTENT OF RUBBER AND THE RATE OF VULCANIZATION.

The contrast between the high nitrogen content of a slow-curing crêpe, compared with the low nitrogen content of fast-curing crêpe from a slab rubber, can only be explained on the

theory that, in the slab rubber, decomposition of the protein or nitrogenous substance takes place. A soluble portion is washed out during crêping, and the insoluble residue, or part of it, is presumably the substance causing acceleration in rate of cure in the case of slab rubbers.

In view of the vulcanizing results obtained in Parts I and II, the authors have analyzed a large number of their samples which are tabulated below, together with the rate of cure determined by the load-stretch curve method.

Per Cent of Nitrogen in Dry Sample.	Optimum Time of Cure in Hours.	Per Cent of Nitrogen in Dry Sample.	Optimum Time of Cure in Hours.	Per Cent of Nitrogen in Dry Sample.	Optimum Time of Cure in Hours.
0.31 .....	2¾	0.42 .....	2¾	0.28 .....	2¼
0.26 .....	1½	0.19 .....	1¼	0.22 .....	1½
0.19 .....	1¼	0.37 .....	2¾	0.31 .....	2¼
0.16 .....	1¼	0.36 .....	2¼	0.19 .....	1¾
0.17 .....	1¼	0.36 .....	3½	0.24 .....	1¼
0.17 .....	1¼	0.35 .....	2¾	0.37 .....	3¼
0.18 .....	1¼	0.38 .....	3½	0.24 .....	1
0.18 .....	1¼	0.20 .....	1¼	0.38 .....	3¼
0.33 .....	2½	0.20 .....	1¼	0.20 .....	1
0.30 .....	1¾	0.40 .....	2¾	0.39 .....	3¼
0.16 .....	1¼	0.19 .....	1	0.26 .....	1
0.11 .....	1¼	0.40 .....	3¼	0.36 .....	3¼
0.13 .....	1¼	0.33 .....	3	0.27 .....	1¼
0.12 .....	1¼	0.23 .....	2¼	0.38 .....	3¼
0.12 .....	1¼	0.27 .....	2½	0.40 .....	3¼
0.18 .....	1¼	0.36 .....	2¾	0.19 .....	2¼
0.17 .....	1¼				

In every case, the amount of nitrogen in a slow-curing rubber, is about 50 to 100 per cent. greater than the amount of nitrogen contained in a fast-curing slab rubber, the amount of nitrogen being determined on all samples after conversion to crêpe and drying.

On the other hand, the amount of nitrogen in samples of rubber prepared by the evaporation of thin layers of latex, or by pouring out the latex into thin layers, after addition of acid coagulant, and allowing the thin sheets thus obtained to dry rapidly, is high, and amounts in some cases to 0.5 per cent. Such samples are rapid-curing, although the percentage of nitrogen indicates that no decomposition of the protein or nitrogenous constituents of the rubber has taken place, the factor de-

ciding rapidity of cure being apparently, in this case, the unknown substance present in the evaporated serum after removal of the major portion of the protein.

#### SUMMARY.

1. The experiments and results of Part I show that one factor which causes variability in respect of rate of cure in plantation Para rubber is produced during the first six days after coagulation and that the change which takes place in the coagulum is progressive during this period, while after this period, no further change, under ordinary conditions, takes place.

2. The action of antiseptics, such as formalin, as well as heat and cold, are also shown to inhibit this change, while soaking of the fresh coagulum in running water considerably retards the rate of cure.

3. The action of formalin is also shown to be partly, though not to any great extent, an action on the accelerating agent after its formation.

4. Experiments on the cold storage of freshly coagulated rubber show that while the change which produces rapidity of cure is inhibited as long as the coagulum remains in cold storage, if the rubber is removed again and allowed to remain, without machining, for a further period (13 days or possibly less) at ordinary atmospheric temperatures (about 85 degrees F. in the Federated Malay States), rapidity of cure is again brought about.

5. All the experiments of Part I suggest that the change which produces rapidity of cure in the rubber is caused by biological agencies, that is to say, micro-organisms entering the latex after collection and remaining in the coagulum, and that the change is probably a decomposition of the protein or nitrogenous substances present in the coagulum, producing an accelerating agent which is a decomposition product of the proteins.

6. The experiments of Part II, on the slow-curing rubbers of various proteins and nitrogenous substances, and their decomposition products, including the proteins from the latex serum decomposed by suitable methods after separation from

the serum, confirm the conclusions from the experimental evidence contained in Part I, and show that the original proteins have little or no effect under the conditions employed, while the decomposed proteins have a marked effect.

7. Experiments with undecomposed evaporated serum, after separation of the proteins coagulated by heat, suggest the presence of a second factor which accelerates the rate of cure, and is due to some substance originally present in the latex.

8. In the case of the author's so-called "slab" rubbers, possibly both factors are responsible for the acceleration of the rate of cure, and it would appear that the second factor may be responsible for the actual superior tensile properties of the rubber. Some evidence to this effect is contained in the comparatively poor quality of the rubbers to which the protein decomposition product has been added, in which the second factor has been removed, and also in the good quality in the case of the evaporated latex samples and the rubber to which the evaporated serum has been added. Further experiments are, however, necessary to confirm this.

9. Experiments with evaporated latex, which contains all the serum constituents and is dried with sufficient rapidity to prevent decomposition of the proteins, also confirm the presence of this second factor.

10. The nitrogen figures given in Part III still further confirm the decomposition theory, that is to say, the production of some substance from the protein which accelerates the rate of cure, the nitrogenous portion which becomes soluble in water and is removed on crêping being non-essential. The high nitrogen content, on the other hand, in rapidly curing rubbers produced by evaporation of the latex, without decomposition of the protein, again confirms the evidence obtained as to a second factor which is probably of a non-nitrogenous nature.

11. These experiments and results also show why it has not been possible hitherto to connect the nitrogen content of a rubber with its rate of cure, since a rapidly curing rubber may have either a low or high nitrogen content, and indicate how previous workers have gone astray, or not gone sufficiently far

in their investigations, in connection with the protein or nitrogenous constituents of latex and rubber.

12. Many other experiments on nearly 1,000 samples of rubber all confirm the above results and conclusions.

13. A further investigation is now being made as to the exact nature of the protein decomposition product, which accelerates the rate of cure, and as to the nature of the second factor responsible for acceleration, together with the numerous subsidiary factors which influence the rate of cure, a number of which have already been investigated.

The authors have since found that the protein left in sheets of average thickness can be decomposed and so produce a more rapidly curing sheet rubber by simply rolling up the sheets after machining in order to retain sufficient moisture content for the bacterial decomposition. This demonstrates that the rapidity of cure of the so-called slab rubber is largely due to the decomposition of protein nominally retained by the rubber, even after rolling to sheet form. These results also show the importance of the rate of drying during early stages, as a factor in the preparation of sheet rubber, in order to have a uniform rate of cure.

Dr. Henry P. Stevens, of London, in conjunction with the late Dr. Clayton Beadle in 1912 first published his work on the rate of vulcanization of plantation rubber. He was the first to show that the nitrogenous or so-called insoluble constituents of rubber affect the rate of cure, and that they could be to some extent replaced by the addition of peptone, casein, etc. Later Stevens showed that the increased rate of cure was due to the formation of nitrogenous bases, probably formed by the putrefactive changes which set in when the unwashed coagulated latex was allowed to stand. He separated these bases as phosphotunstates and proved their efficiency as vulcanizing accelerators by adding them to ordinary crêpe rubber and showing the increase in rate of cure produced.



## CHAPTER V.

### ORGANIC AND INORGANIC ACCELERATORS.

THE following summary represents an effort to classify the principal nitrogen-bearing accelerators in a logical manner, and to record concisely their characteristics and efficacy as described by R. Ditmar and translated into French for "*Le Caoutchouc et la Gutta-Percha*," by Georges Noyer; Andrew H. King in "*Metallurgical and Chemical Engineering*"; S. J. Peachey and Douglas F. Twiss in "*The India Rubber Journal*"; and others.

Whatever may be the future of synthetic rubber, the investigations in connection with it led to the discovery of organic accelerators which have revolutionized several lines of rubber manufacture. It was found that synthetic rubber could not be vulcanized without the presence of certain organic catalyzers to facilitate the union of rubber and rubber-like substances with sulphur, and when all natural rubber was substituted the increased rapidity of vulcanization was truly remarkable. The difficulty, as for a time with plantation rubbers, appears to have been the absence of certain so-called impurities found evenly distributed throughout Para rubber coagulated by the Amazon method. These natural catalyzers of rubber latex are believed to be decomposition products and related to the proteins. It is certain that all organic accelerators yet known are nitrogen-bearing and many have amino groups, so that the function of nitrogen appears to be important.

Manufacturers who had been using the old, well-known mineral accelerators began to experiment with these new organic catalyzers and found that they could double their output without expensive increase of steam pressure or danger of impairing the product by high temperature. Those engaged in the production of cheap molded goods discovered that by employing both high temperatures and catalyzers their increased output would take care of overhead.

While this most important recent development in rubber chemistry is still in its infancy, there is already considerable



generalization and a goodly amount of definite facts on which to build. It is thought that, unlike the mineral accelerators which undergo no chemical change during vulcanization, an organic catalyzer unites with one of the reacting substances and forms an unstable compound which then reacts with the other substance. Meanwhile the catalyzer is set free and the entire process is repeated. From a mechanical standpoint a catalyzer is most conveniently mixed with a solid capable of being very finely pulverized. A high boiling point is essential to prevent vaporizing during vulcanization and consequent spongy appearance, known as "blowing."

The most important organic accelerators are as follows:

Aniline oil.	Sodium amide.
Carbon bisulphide addition products with:	Naphthylenediamine.
Aniline.	$\beta\beta$ Dimethyl $\Delta$ trimethyleneamine.
Diphenylthiourea or thiocarbanilide.	Trimethyleneamine.
Dimethylaniline.	Benzylamine.
Tetrahydropyrrole.	Nitroso dimethylaniline.
Dimethylamine.	Piperidine and derivatives:
$\beta\beta$ Dimethyl x methyl trimethylene amine.	Piperidine or aminopentane.
Ammonium compounds:	Methyl piperidine.
Ammonium borate.	Quinoline derivatives:
Aldehyde ammonia.	Quinoline sulphate or quinoline sulphonic acid.
Quaternary ammonium bases.	Quinosol.
Amino compounds:	Oxiquinoline sulphide.
Accelerene or paranitroso dimethylaniline.	Miscellaneous:
Para-phenylenediamine.	Anthraquinone.
Tetramethylenediamine.	Antipyrine.
Hexamethylene-tetramine or hexamethyleneamine or formin.	Naphthylamine.
	Urea derivatives.
	Anilides.
	Formanilide.
	Thioformanilide.

Several of these accelerators are covered by patents and must be purchased through certain dealers who are prepared to quote to the consumer prices inclusive of the license fee of the patent owners.

The catalyzers in question are piperidine and methyl piperidine, tetramethylenediamine, hexamethylene-tetramine, thiocarbanilide, and aniline hydrochloride. The first three of these are not made in the United States at present.

#### ANILINE.

*Aniline.*—This material, described in Chapter XI, has been extensively employed as an accelerator in rubber work for a

number of years, particularly in the manufacture of automobile tires and tubes.

To obviate the poisonous effects of aniline it is essential to protect the workmen by the use of waterproof outer garments, such as rubber shoes, gloves and aprons to prevent the absorption of the liquid by contact with the skin. In addition it is also necessary to remove thoroughly and rapidly all aniline fumes arising from the warm rubber during the milling and calendering and generally by ventilation to provide an abundance of fresh air in the work rooms.

#### CARBON BISULPHIDE ADDITION PRODUCTS.

*With Aniline.*—Diphenylthiourea, or thiocarbanilide, is one of the earliest known organic accelerators. It takes the form of large colorless tablets melting at 154 degrees C., and is a very efficient catalyzer, particularly for quick-curing stocks, because it does its work at the very beginning of vulcanization. The proportions used vary from  $\frac{1}{2}$  to 3 per cent.

*With Dimethylaniline.*—Cited by Ditmar and King.

*With Tetrahydropyrrole.*—Known as pyrrolidin in Germany. Cited by Ditmar and King.

*With Dimethylamine.*—This substance gives an active addition product. With Para, 100 per cent. sulphur and the addition of 1 per cent. of the compound of carbon bisulphide and dimethylamine vulcanization takes place completely with 15 minutes' cure at 135 degrees C. (German patent 269,512.)

*With  $\beta\beta$  Dimethyl  $\alpha$  methyl Trimethylene Amine.*—Cited by Ditmar.

#### AMMONIUM COMPOUNDS.

*Ammonium Borate.*—This noticeably effects the cure, but the fact has only scientific interest, according to Ditmar.

*Aldehyde Ammonia.*—This very satisfactory catalyzer is readily soluble in water, sparingly soluble in alcohol, and almost insoluble in ether. It melts between 70 and 80 degrees C. and sublimes without decomposition at 100 degrees C. Its efficacy as an accelerator, according to King, may be seen in the fact that 100 parts Para, 10 parts sulphur, and 1 part aldehyde ammonia will cure in 30 minutes at 45 pounds steam pressure, 140 degrees C. (Ditmar says 1 hour at 3 atmospheres—42

pounds—while without the accelerator 2 hours would be required), whereas 90 parts Para, 9 parts sulphur, and 1 part lime require 85 minutes at the same pressure for a cure.

*Quaternary Ammonium Bases.*—These are covered by Bayer & Co.'s patents of 1914, together with aldehyde ammonia, para-phenylenediamine, sodium amide, benzylamine, and naphthylenediamine, all rapid accelerators.

#### AMINO COMPOUNDS.

*Accelerene.*—This widely used English catalyzer is among the most powerful known accelerators. When used in the proportion of  $\frac{1}{3}$  to  $\frac{1}{2}$  of 1 per cent. it reduces the required period of vulcanization to one-third normal with highly satisfactory results; and in conjunction with certain other familiar substances in quick repair compounds reduces the period of cure to one-eighth normal. Cheap mixings containing considerable reclaim or waste, particularly if golden antimony sulphide be present but no free sulphur, do not respond so readily as medium and high-class mixings. In such cases sufficient free sulphur must be added and the proportion of antimony sulphide may be reduced to that needed to give the desired color, after which the usual acceleration will be attained. In the manufacture of vulcanite the addition of  $\frac{3}{4}$  of 1 per cent. of accelerene to a mixture consisting of 100 parts rubber and 40 parts sulphur reduced the period of vulcanization from 6 to 2 hours, yielding a hard and very durable product.

Essentially paranitroso dimethylaniline, and wholly different from the German type of accelerators, accelerene owes its activity to the presence of the nitroso group, and not to feeble basic properties. Aside from its high acceleration it possesses several characteristics in use that are of great value. Goods vulcanized in its presence show somewhat greater tensile strength, probably due to the diminished degree of depolymerization possible in so short a period of heating. Vulcanization stops when the goods are taken from the pan or press, so they suffer little deterioration in storage, tests demonstrating this now covering a period of two years. Sulphuring-up may also be entirely prevented by its use, though at the sacrifice of acceleration. The quantity of sulphur may be reduced to 3 or  $3\frac{1}{2}$  per cent.;

$\frac{1}{2}$  per cent. of accelerene is then added and the mixing cured in the ordinary manner. As employed for this purpose the catalyzer facilitates a complete combination of rubber and sulphur, with the result that little or none of the latter remains in the rubber.

*Para-phenylenediamine*.—This very poisonous catalyzer melts at 140 degrees C., sublimes without decomposition at 267 degrees C., is readily soluble in alcohol and ether, and moderately so in water. In Bayer & Co.'s German patent No. 280,198, January 1, 1914, it is stated that this accelerator gives good satisfaction with synthetic rubber, 100 parts isoprene rubber having been cured completely upon being mixed with 10 parts sulphur, 2 parts para-phenylenediamine and being heated in a press for 15 minutes, at 45 pounds steam pressure.

*Tetramethylenediamine*.—Known also as putrescine, this is a natural product of protein decomposition formed during the putrefaction of animal matter such as fish. It is produced chemically by Bayer & Co.

*Hexamethylene-tetramine*.—Known also as *Hexamethyleneamine* and *Formin*. This accelerator is largely used. It comes as a fine white crystalline powder. The U. S. P. grade is free of moisture while the so-called technical grade usually contains about two and one-half per cent. of water.

It is very soluble in water and as it vaporizes freely in the operations of mixing and calendering it occasions considerable trouble in the form of a rash or eruption on the skin, particularly on exposed surfaces moistened with perspiration. The use of gloves, and otherwise protecting exposed portions of the body, minimizes the annoyance.

*Miscellaneous Amines*.—Other amino compounds cited by King as of lesser importance yet having some accelerating power include: sodium amide (rapid acceleration according to Ditmar); naphthylenediamine (rapid acceleration according to Ditmar); trimethyleamine, benzylamine (rapid acceleration according to Ditmar);  $\beta\beta$  dimethyl  $\Delta$  trimethyleamine, and nitroso dimethylaniline.

#### PIPERIDINE AND DERIVATIVES.

*Piperidine*.—A liquid miscible in water in all proportions, having a specific gravity of .881 at 0 degrees C., boiling at

105.7 degrees C., and smelling like pepper and ammonia. This, the prototype of the more recently discovered organic catalyzers, was brought out and patented by Bayer & Co. in 1912, for use in the manufacture of synthetic rubber, but its extraordinary value as an accelerator in connection with natural rubber for both hard and soft rubber articles soon overshadowed its original purpose. A mixture of 100 parts Para and 10 parts sulphur that requires an hour to cure at 53 pounds steam pressure, may be cured perfectly with only 15 minutes' heating by the addition of  $\frac{1}{2}$  part of piperidine. The product obtained from this compound contains about 3.5 per cent. of combined sulphur. Piperidine may also be used for producing hard rubber by adding 25 per cent. sulphur. (German patent No. 266,618.)

*Methyl Piperidine.*—This active catalyzer boils at 107 degrees C.

#### QUINOLINE DERIVATIVES.

*Quinoline Sulphate.*—Also known as quinoline sulphonic acid. An excellent accelerator yielding good-looking well-vulcanized rubber. King suggests that the potassium salt of this acid might give better results.

*Quinosol.*—This accelerator takes the form of sulphur yellow needles soluble in both alcohol and water. It is manufactured by Frisch, of Hamburg, Germany, and mixes easily with rubber compounds before vulcanization. In a mixture of Peruvian rubber, 12 kilograms; white substitute, 19 kilograms; Kaolin (China clay), 2 kilograms; chalk, 5 kilograms, and sulphur, 4.5 kilograms, the accelerating effect, according to Ditmar, is not great, but quinosol acts quite differently when mixed with litharge and crude rubber free of substitute, the combined effect being greater than the sum of the effects of each employed alone.

*Oxiquinoline Sulphide.*—This is a satisfactory but too active accelerator. It can be used with all sorts of compounds because it answers all the needs of the industry. In tests conducted by Ditmar in collaboration with the Japanese chemist Nawa-Naami, a mixture containing Peruvian rubber, 40 kilograms; brown rubber substitute, 10 kilograms; paraffin, 5 kilograms; chalk, 41 kilograms; and sulphur, 4 kilograms, re-



quired 2 hours' heating at a pressure of 4 atmospheres (56 pounds). With oxiquinoline sulphide the mixture was vulcanized in 50 minutes. With quinoline sulphate 75 minutes were required. Tests of accelerated and unaccelerated products showed the same breaking point, but the elongation of the accelerated product was found to have been reduced one-half.

#### MISCELLANEOUS.

*Anthraquinone*.—Recommended in 3 to 5 per cent. strength in batches containing rubber substitute. In a typical mixture containing rubber substitutes it reduces the duration of vulcanization from 2 hours to one-half hour.

*Antipyrine*.—Acts like anthraquinone. (Ditmar.)

*Naphthylamine*.—Acts like anthraquinone. (Ditmar.)

*Urea*.—This and such derivatives as guanidine have been found useful. (King.)

*Formanilide*.—Many patents cover the anilides, such as formanilide.

*Thioformanilide*.—Cited by King.

*Albumen*.—The direct addition of proteins to rubber, as described by W. Esch in German patent No. 273,482, November 22, 1912, presents an interesting possibility. The protein, usually egg albumen, 15 parts, is mixed with 2 parts hydrated lime or magnesium hydroxide to form a paste. Low grades of rubber, when mixed with this paste, dried, sheeted and smoked to render the albumen insoluble, are considerably improved thereby.

*Magnesia*.—Marckwald and Frank claim that:

1. Magnesia affects vulcanization only by forming intermediate products which accelerate the combinations of sulphur with rubber.

2. Owing to decomposition of the chloride (left in through inefficient washing) by exposure to the air, and also during vulcanization, magnesium chloride and sulphate form undesirable contents in cold vulcanized goods.

In cold cure with chloride of sulphur vapor sulphur in the mixing has no more immediate influence than any other filler—although a later action may perhaps be expected in a warm, light warehouse.

The following accelerating preparations are patented by Dr. D. F. Twiss:

*Quicklime* slaked with a solution of sodium or potassium hydroxide and the resulting soda or potash lime employed as a fine powder. Suitable proportions are found to be ten parts of quicklime to three parts of sodium hydroxide or four parts of potassium hydroxide. By using one per cent. of such a powder in a rubber mixing, the alkali hydroxide can be more evenly distributed than if used alone.

Another method is to use the caustic alkali in conjunction with an organic solvent such as glycerol. If this is heated to about 175 degrees C. to expel superfluous water, the hydroxide can be dissolved and alkali glyceroxide obtained. Potassium hydroxide is found somewhat preferable for this method and also for the quicklime one. One part of potassium hydroxide may be used with four parts by weight of glycerol, although the proportions may be widely varied. One or two per cent. of such a solution may be mixed into rubber uniformly and there is no tendency to produce porosity of the rubber; but the vulcanization process is greatly accelerated, the effect being comparable with that of the strongest organic accelerators. It is also noteworthy that the actual quantity of alkali approximates closely to the one-half per cent. recommended for the most effective organic accelerators and that with a rubber-sulphur mixing the resulting vulcanized rubber in both cases possesses the same clear, dark, almost semi-transparent appearance.

A mixture of rubber with five per cent. of the solution, when cured for 90 minutes at 40 pounds pressure, undergoes complete vulcanization, practically no sulphur remaining uncombined. Other organic compounds may be employed for the solution of the alkali, such as glycol. As to aging of samples vulcanized in the presence of the alkali solution of glycerol, after a lapse of three years since vulcanization a certain weakening was observed, but no greater than in similar mixings containing other accelerators.

The following are trade designations of secret compounds used as accelerators, based on ingredients mentioned in this chapter: Acelemal, Annex, Anvico, Dry Aniline, Duplex, Ex-

cellerex, M. C. C., Paradin, Tensilite, Velocite, Velosan, Vitaminex, Vulcavit.

#### SUMMARY.

The list of organic vulcanization accelerators employed in American rubber manufacturing practice is not as long as the foregoing description would indicate. Practical consideration of price and demonstrated utility confines the list substantially to the following:

Thiocarbanilide.

Hexamethylene-tetramine.

Aniline.

Accelerene or paranitroso-dimethylaniline.

Para-phenylene-diamine.

Aniline was at first the most extensively used accelerator but seems to have given place in general usage to thiocarbanilide due to the inconvenience of its liquid form and its pronounced poisonous nature.

Thiocarbanilide is offered to the rubber trade under numerous trade names.

Hexamethylene-tetramine is nearly as popular an accelerator as thiocarbanilide. It imparts a characteristic firmness and snappy quality to vulcanized rubber and in poisonous quality is not as dangerous as aniline although responsible for an annoying skin irritation particularly noticeable in warm weather.

## CHAPTER VI.

### FILLERS AND INGREDIENTS USED IN RUBBER COMPOUNDS.

INDIA RUBBER is compounded for two reasons, the first being to reduce the cost without destroying the usefulness of the gum, the second being to impart qualities possessed by a great variety of mineral, vegetable, and even animal substances.

AGALMATOLITE.—A silicate of aluminum resembling soapstone. It has no advantages over talc, silicate of magnesia, or soapstone in rubber use. Its specific gravity is about 2.25.

ALUMINA.—The oxide of aluminum and a chief constituent of clay. Its specific gravity is 4.15. Ordinarily speaking, it is a very inert substance, insoluble, and not readily attacked by acids. It is best known in the arts under the forms of corundum, emery, etc. As obtained chemically it is a fine white glistening powder, harsh and dry to the touch. Eaton's formula for the use of oxide of aluminum in making white rubber was india rubber 40 per cent., oxide of aluminum 55 per cent. and sulphur 5 per cent.

ALUMINITE.—A white clay containing a large percentage of aluminum (about 30 per cent.) and a certain amount of silica. Its specific gravity is low, and its fusing point 2,400 degrees F.

ALUMINUM FLAKE.—A natural product (aluminum silicate) in the form of a white powder, free from grit, with a specific gravity of 2.58. It is a remarkable heat resistant, is inert in compounds, and toughens them. It is a partial substitute for zinc oxide, both for color and strength.

ALUMINUM OXIDE.—See Alumina.

ALUNDUM.—A patented abrasive material made from oxide of aluminum or bauxite.

AMPHIBOLINE.—A German earth. When wetted and dried, it will not absorb water again. Specific gravity about 3.25. It is used in waterproofing, the product being non-inflammable. It is mixed with gelatine or size, no rubber being used: 34 parts

amphiboline, 9 parts gelatine, 2 parts chrome alum, 2 parts ammonium sulphate, 53 parts water.

**ANHYDRITE.**—The water-free form of sulphate of lime or gypsum, white in color and crystalline in form. Its specific gravity is 2.9. It is formed artificially by heating gypsum so as to drive off all its water. Gypsum that has been over-heated in the preparation of plaster of Paris and that has lost its ability to “set” is pure anhydrite. It is used as a filler in rubber compounding instead of whiting or Paris white.

**ANTIMONY.**—See Golden Sulphuret of Antimony, Black Antimony, and Kermes.

**ANTIMONY OXIDE.**—There are really three of these oxides. The trioxide, one most useful in the arts, is a snow-white powder of the specific gravity of 5.2. It may be obtained by treating stibnite or, better still, powdered antimony metal with nitric acid, in a current of air sufficient to carry off the copious fumes arising during the operation, or by treating the chloride of antimony with cold water for several days. A mixture of the trioxide with a small percentage of the insoluble peroxide may be obtained by melting antimony in a cast iron retort fitted with nozzles, through which air may be blown to agitate the melted metal. Dense white fumes arise, which may be condensed in suitable chambers into a snow-white powder. This is used in coloring dental vulcanite.

**ARGILLACEOUS RED SHALE.**—A shale that has a large amount of clay in it is termed argillaceous, and the substance mentioned in the heading may be briefly termed clay tinted red with oxide of iron. The analysis of argillaceous clay shows: alumina 39, silica 46, water 13, iron, magnesia, and lime 2. It was the basis of a well-known oil-resisting compound that for years baffled imitation. Specific gravity 2.70.

**ARSENIC.**—A white brittle metal, with a specific gravity of 4.7 or 3.7, according to its form. Also a popular term for the oxide of arsenic, sometimes called the white arsenic, which is a heavy white powder of the specific gravity 3.7. It is slightly soluble in cold water and to the extent of 10 per cent. in hot water. There are several coloring matters formed from arsenic. The most familiar are Paris green; realgar, which is red, and orpiment, yellow. The white oxide is rarely used; the



red sulphide is, however, often used; the green has been used in mechanical rubber goods, but the color was not a valuable one. Hancock vulcanized gutta-percha with orpiment, and Forster used it in "mosaic work" for floor coverings. An anti-fouling composition for ships' bottoms is formed of gutta-percha, copper, bronze, and arsenic. Another is formed of: india rubber 2 pounds, rosin 7 pounds and arsenic 2 ounces.

ASBESTIC.—The part of the rock remaining after the richer veins of asbestos have been extracted. This remainder is a purely fibrous material, clearly showing its origin. For mechanical uses it is ground fine, and for all sorts of fire-proofing purposes is valuable and much cheaper than long fiber asbestos. It makes an excellent compounding material for asbestos packings, etc., in connection with rubber.

ASBESTINE.—A pure fibrous silicate of magnesia, called also mineral pulp. It is mined near Gouverneur, New York, where is the only deposit at present known where magnesia shows so distinct a fiber. Apparently the pulverized mineral is a very strong white powder, but in actual use it has not much more covering quality than whiting. It was at one time used largely in the manufacture of rubber shoes, but, aside from being inert and a good filler, was probably no better than whiting, while it was more costly. It is often used in white goods, in connection with oxide of zinc, to make a light weight compound. It is also known as agalite and asbestine pulp. Its composition is: silica 62, magnesia 33, water 4, iron oxide and alumina 1. Specific gravity 2.80.

ASBESTOS (*Amianthus*).—A fibrous silicate of calcium and magnesia, also called stone flax, salamander's wool (from an old belief that it was originally made from the wool of the salamander), cotton stone, mountain flax, mountain wood, and mountain cork. Its specific gravity is 3.02 to 3.1. An analysis of the two best known varieties shows:

	Canadian.	Italian.
Silica .....	40.92	40.25
Magnesia .....	33.21	40.18
Water of hydration .....	12.22	14.02
Alumina .....	6.69	2.82
Protoxide of iron.....	5.77	.75
Soda .....	.68	1.37
Potash, etc. ....	.22	.15
Sulphuric acid .....	traces	.31

The longest fiber is possessed by the Italian, which is sometimes 3 feet in length. The Canadian ranges from 3 to 6 inches in length, but it is finer, more flexible, and more easily separated than the Italian. The mineral divides itself naturally into three classes: the first, coarse, brittle, very plentiful, and cheap; the second, possessing well-defined fibers of a brownish-yellow color, fragile, and containing many foreign bodies; the third, with pure white silky fibers which can be woven into textiles. A notable use to which asbestos has been put is in the production of packing and brake linings. Its low heat conductivity renders it particularly useful in steam packings, both for cylinder work and for joints, while its incombustibility has long caused it to be used for fireproofing purposes. There are fibers formed of serpentine rock which are much used as a substitute for genuine asbestos, and answer nearly as well, being, however, shorter in fiber and somewhat less durable.

ATMIDO.—A snow-white filler of low specific gravity, free from organic matter and indifferent to acids. Used in small proportions, is said to increase both strength and resiliency in soft rubber goods. Used in large proportions, it makes a very hard compound, said to resist superheated steam. Of German origin.

ATMOID.—A very light white earthy matter of English origin. Analysis proves it to be an almost pure silica—quite close, in fact, to infusorial earth. Specific gravity 2.00.

BARIUM CARBONATE.—See Carbonate of Barium.

BARYTES.—A heavy white mineral that in commerce takes the form of a fine white or gray powder. It is obtained by grinding the mineral heavy spar, or by chemical means from barium chloride. Its specific gravity is 4.5. It occurs in commerce under the names "permanent white" and "blanc fixe." The artificially prepared substance is to be preferred to the finely ground mineral, on account of its less crystalline form. The commercial article should always be examined to determine its freedom from acid impurities. Barytes is chiefly used as an adulterant for white lead and paints. Thus, Venice white contains equal parts of sulphate of barytes and white lead; Hamburg white, 2 parts to 2 parts of white lead; and Dutch white, 3 parts to 1 part of white lead. It is wholly inert when

used as an ingredient in rubber compounding, increases the resiliency of rubber, and is a make-weight.

**BASOFOR.**—A trade designation for a specially precipitated barium sulphate or “blanc fixe.” Used as an inert filler and pigment. See Barytes.

**BLACK ANTIMONY.**—A black powder obtained by grinding stibnite or antimony ore. It is a sulphide of the metal and is met with more or less pure, as it is often prepared from a high-grade ore. The sulphur contained in it is unavailable for vulcanizing purposes, and if used in compounding it is necessary to add a sufficiency of sulphur to vulcanize. In the purest form, black antimony contains about 28 per cent. of sulphur and 72 per cent. of antimony. It is insoluble in water, but is dissolved by muriatic acid or by caustic alkalis. From its solution in alkali a fine brown-red powder may be obtained by treatment with a dilute acid, and this powder, known as kermes, has the same chemical composition as that mentioned above. Its specific gravity is 4.6. It was formerly used sometimes as a filler, as it was believed to give a soft effect in molded goods. It has been almost wholly displaced, however, by cheaper and better ingredients.

**BLACK LEAD.**—See Plumbago.

**BLANC FIXE OR PERMANENT WHITE.**—Artificial barium sulphate, specially prepared by precipitation from solutions of native barytes. There are several methods giving variations in product adapting it to specific purposes. The specific gravity is 4.10-4.20. The grain is extremely fine and amorphous. It is particularly valuable as a filler and is said to enhance the tensile strength of rubber. See Barytes.

**BLUE LEAD.**—Where zinc ores are found in combination with galena, or natural sulphide of lead, the two are often smelted together with raw coal and slaked lime, producing a fume called blue powder, which is sold under the name of blue lead. It is an excellent filler, but is not as good as sublimed lead, for example, as it does not impart enough resiliency to rubber. Its chief merit is its cheapness. A very fine quality of blue lead, containing considerable lead oxide, is now on the market, but this must not be confused with either of the two low-grade articles mentioned in these paragraphs. This blue

lead is of exceeding fineness, and gives a peculiarly soft finish to the rubber. Used in the place of litharge, it materially assists in the cure, and produces a fine black. As it has a high specific gravity, it often displaces barytes. Blue lead is also a name given to an artificial aluminous substance occurring either as a loose powder or in a concrete form, colored blue by means of some kind of blue dye—aniline or logwood—which does not contain lead.

BONE ASH.—See Calcium Phosphate.

BONEBLACK.—See Charcoal (Animal).

BUCARAMANGUINA.—A transparent amber-colored, combustible material, found near Bucaramanga, Colombia. It is somewhat similar to asbestos, for which it has been mentioned as a substitute in the manufacture of packings.

BURNT UMBER.—An earth containing a large amount of iron oxide of a dark-brown rust color. As mined, it is called raw umber, and the product obtained by calcining it is known as burnt umber. It was formerly used in brown packings, and to a certain extent, in maroon goods.

CALAMINE.—An ore of the metal zinc, and a carbonate of zinc. Ordinary calamine, which is a silicate of the metal, has a specific gravity of 3.6 to 4.4, and is little used in the arts. Noble calamine, or native carbonate of zinc, is a gray or grayish yellow to brown powder, according to its priority. Its specific gravity is 3.4 to 4.4. Its nature is earthy, and heat has no action upon it. A little of it is said to toughen soft compounds.

CALCIUM CARBONATE.—Very familiar under the native form of limestone, marble, or chalk. See Whiting.

CALCIUM PHOSPHATE OR PHOSPHATE OF LIME.—The chief constituent of bones, forming the bulk of their ashes when burnt. It is a white powder, and when in crystalline mineral form, has a specific gravity of 3.18. It is insoluble in ether, alcohol, or the benzene class of solvents. As it occurs naturally it is known as flour of phosphate and is used in part as a substitute for whiting. Bone ash made from animal charcoal is a common form used in the same way.

CALCIUM SULPHATE.—Also called gypsum. A common mineral occurring under various forms and names as alabaster, selenite, and gypsum earth. It is pure white in color and has

a specific gravity of 2.33. Plaster of Paris is a calcined form of gypsum. In the ordinary recovery of rubber by the acid process, whiting becomes changed from carbonate to sulphate of calcium, otherwise sulphate of lime. See Plaster of Paris and Anhydrite.

**CALCIUM WHITE.**—Another name for whiting.

**CALOMEL.**—A white, inodorous powder of specific gravity about 7.2. It is permanent in the air, but should be kept in the dark, as light blackens it. When pure, it may be wholly volatilized by heat. Calomel blackens under the action of alkalis. It is insoluble in water, alcohol, ether, or benzine. It is the basis of a compound for rendering hose waterproof, the other ingredients being magnesia, black antimony, oxide of zinc, tar sulphur and india rubber. Its function in rubber is to hasten the cure.

**CARBONACEOUS CLAY.**—Found near Lake Albert, South Australia. After being boiled at a high temperature with caustic soda and washed with a weak solution of sulphuric acid, it assumes a remarkably light, spongy, elastic character. It is used as an absorbent, and as a substitute for cork in linoleum. It has been suggested as an ingredient for use in connection with rubber for playing-balls, etc.

**CARBONATE OF BARIUM.**—Known also as witherite; has a specific gravity of 4.3. It is a white powder insoluble in water and alcohol. See Barytes.

**CARBURET OF IRON.**—A name given to a mixture of graphite and oxide of iron. A fine black-brown powder, specific gravity 4.00, although variable. It makes a fair filler in compounding, being inert and strongly coherent. In packings it has been largely used, and also in compounds for wagon covers and tarpaulins before reclaimed rubber came largely into use. It has also been used in cements for card clothing.

**CHALK.**—A white, soft, somewhat gritty substance, consisting chiefly of carbonate of lime. It is made up of myriads of very small shells of marine animals long extinct. Its nature is earthy; that is to say, it is not easily affected by ordinary bodies. Acids disengage carbonic acid gas from it. Its specific gravity is 2.9. If heated to a red heat, carbonic acid gas escapes and quicklime is left behind. See Whiting.



**CHARCOAL (ANIMAL).**—Animal charcoal is made from bones distilled out of contact with air and has the property, in a high degree, of absorbing odors and soluble coloring matters. It is often used, therefore, in deodorizing rubber goods, and experimentally by chemists for filtering gutta-percha dissolved in bisulphide of carbon, where a perfectly clear product is desired. Its use is advised by Forster in gutta-percha compounds, and by Warne, Jaques, and others for packings to withstand heat. Its specific gravity is about 2.85.

**CHARCOAL (VEGETABLE).**—This is a popular term for the coal produced by the charring of wood. There are many materials which are really charcoals, such as animal charcoal just quoted, carbon, coke, graphite, and wood charcoal. All of these are practically the same in their pure states, being almost wholly carbon. Wood charcoal—that which is meant in rubber compounding by vegetable charcoal—consists of carbon, hydrogen and oxygen, the last two being in the proportion to form water. It is black and brittle, insoluble in water, infusible, and non-volatile in the most intense heat. It has the power of condensing gases and destroying odors. Charcoal may or may not be a bad conductor of heat and a good conductor of electricity, these properties depending upon the wood from which it is made. Technically, it is divided into hard wood charcoal and soft wood charcoal. Its composition at ordinary temperatures is about as follows: carbon 85 per cent., water 12 per cent., ash 3 per cent. Specific gravity (powdered) 1.40 to 1.50. It is used in rubber compounding in certain vulcanite varnishes and in certain insulated wire compounds. For the latter use, willow charcoal is preferable, as it is a decided non-conductor. It has also been used in sponge rubber, with the idea that it acts as a preservative in a compound which is very likely to be short-lived. Macintosh used large quantities of ground charcoal in place of lampblack in some of his compounds. A French substitute for vulcanite paints or lacquers is made of 10 pounds of bitumen, 15 parts of charcoal, and a little linseed oil, mixed by heating.

**CHINA CLAY.**—See Kaolin.

**COMPO.**—A name for a composition used in rubber manufacture in the United States years ago, but not in use now. The name, however, clings to two compounds sold by an

English chemical house for use in rubber work. They are of a secret nature. No. 1 is used in the manufacture of oil-resisting valves and in tubing for chemical factories, in the proportion of 30 pounds of compo to 10 pounds of rubber. No. 2 is used for soles for tennis shoes and in mechanical goods, in the proportion of 25 pounds of compo to 10 pounds of rubber.

CORK is the bark of the cork oak, native of Southern Europe and Northern Africa. The chief supplies come from Spain and Portugal. Cork is the basis of the fine black known as Spanish black, which is made by burning the refuse in close vessels. In granulated or powdered form, cork has long been a favorite ingredient in rubber compounding. Not that it is used in any such measure as whiting or barytes, but many mills have used it, and a few in large proportions. Used in connection with india rubber and gutta-percha, it has been the subject of about fifty patents. Its largest use, perhaps, was in the manufacture of kamptulicon, where india rubber is used as a binding material, and in linoleum, where oxidized oils are used in place of rubber. It was also used in what was known as leather rubber, in which palm oil distillate, a little india rubber, and a good deal of granulated cork were used. At one time it was also compounded with rubber and made up into a waterproof felt for hats. It also went into compounds to resist heat, into cricket balls, and into golf balls, where it was compounded with gutta-percha and enough metal filings were added to give the necessary weight. A rubber blanket used in special manufacture also had its surface covered with granulated cork as an absorbent material. In some cases the cork was charred and roasted to remove what resinous matter might be in it, while in others resinous matter was removed by boiling in alcohol. In its usual form cork has a specific gravity of 0.24. Fine grinding eliminates much of the contained air with proportionate rise in specific gravity.

CORNWALL CLAY.—See Kaolin.

CORUNDUM.—A mineral which is nearly pure alumina, yet of great specific gravity, and of exceeding hardness, being inferior, in this respect, only to the diamond. Emery (which see) is a variety of Corundum. Specific gravity 3.90.

DIATOMACEOUS EARTH.—See Infusorial Earth.

ELECTRIC FINISH.—See Farina.

EMERY.—The average composition of emery may be taken as alumina 82, oxide of iron 10, silica 6, lime  $1\frac{1}{2}$ . Its specific gravity is about 3.8 to 4. It is prepared by breaking the stone at first into lumps about the size of a hen's egg, then running it through stamps, and crushing it to powder. It is then sifted to various degrees of fineness, and graded according to the meshes of the sieve. Emery is next in hardness to diamond dust and crystalline corundum, and it is used chiefly as an abrading agent. Prior to the invention of vulcanite, emery wheels were made by heating clay and emery in suitable molds, thus vitrifying them like common earthenware. In rubber mills it is chiefly used in the manufacture of what are known as vulcanite emery wheels. It is also used in grinding and sharpening compounds, as hones and strops. (See also Alumina and Corundum.) A certain amount of it also gives the desired surface to rubber blackboards.

FARINA.—This is sometimes used in small quantities in unusual mixtures as a compound, but has little value, as there are many better substitutes for it. A practical use for it, however, is the brushing of a rubber surface with it before vulcanization, when it is necessary to have printing or stamping done upon that surface afterwards. Farina is made largely of potatoes, another name for it being potato starch. The process consists simply of crushing, sifting, washing, bleaching, and grinding, which is repeated three times, and each time the starch granules separate and are collected. It has a specific gravity of 1.50. Potato starch will be remembered by rubber manufacturers as the material which the gossamer makers used successfully for a number of years in the production of the "electric" or "corruscus" finish. Bone ash is used sometimes in the place of farina, where rubber surfaces are to be printed upon.

FELDSPAR.—A name given to a group of silicates of which the principal ones are orthoclase or potash feldspar, containing silica, alumina, and potash, and having a specific gravity of 2.5; albite, containing silica, alumina, and soda, specific gravity 2.61; oligoclase, containing silica, alumina, soda, and lime, specific gravity 2.66; and anorthite, containing silica, alumina, and lime, with a specific gravity of 2.75. The feldspars by the action

of the weather break down into china clay, kaolin, or pottery clays. Ground very fine, they have been used in the production of rubber enamels and lacquers.

**FIRE CLAY.**—A kind of clay which, better than any other, resists the action of heat and direct flame. It is composed principally of silica and alumina, with traces of the alkali earths. The best is found in conjunction with coal, and is called Stourbridge clay. Its specific gravity is about 2.5, and its color dirty white. Mixed with vulcanized india rubber dissolved in tar oil and sulphur, it forms a compound which, when applied to hot joints, cures at once.

FLINT is practically pure silica and its specific gravity is 2.63. The nature of the powder obtained by grinding is always sharp and gritty. It is unacted upon by all ordinary means, and with difficulty even in the laboratory of the chemist. Its principal use, perhaps, is in the manufacture of glass. Flint varies in color from yellow and brown to black. It has been used in erasive rubbers, although pumice stone is better.

**FLOUR OF GLASS.**—Glass powdered and sifted through a fine sieve of 150 meshes to the inch. Glass varies much in its composition, the more common kinds containing lime, while the so-called flint glass contains lead. Potash and soda also enter into the composition of glass; hence all flour of glass will contain those ingredients which entered into the composition of the glass it was obtained from. Its specific gravity ranges from 2.40 to 3.00 for ordinary compositions. Generally speaking, flour of glass may be considered an inert substance under ordinary conditions, though the softer kinds are attacked even by boiling water. It was used by Newton and Wray in insulated wire compounds, and has also been used in certain packings.

FLOUR OF PHOSPHATE.—See Calcium Phosphate.

FOSSIL FARINA, also called mountain milk, is an earth physically similar to infusorial earth. It is obtained from China and consists of silica 50½, alumina 26½, magnesia 9, water and organic matter 13, with traces of lime and oxide of iron. It has been used in rubber compounding for the production of packings and semi-hard valves.

FOSSIL MEAL OR FOSSIL FLOUR.—See Infusorial Earth.

**FRENCH CHALK.**—This is ground and sifted talc, forming a white, greasy-feeling powder. Its chemical composition is hydrated silicate of magnesia, the water being chemically combined. Its specific gravity is 2.70. See Talc.

**FULLER'S EARTH.**—A kind of clay. It is a greenish or brownish earthy, somewhat greasy-feeling substance, having a shining streak when rubbed. Its composition is: silica 70, oxide iron 2.5, alumina 3.5, lime 6, combined water 16, magnesia trace, phosphoric acid trace, salt 2, alkalies trace. Fuller's earth is found in extensive deposits in England, where its annual consumption at one time exceeded 2,000 tons, chiefly in woolen manufacture for fulling cloth. Its specific gravity is from 1.8 to 2.2. It is used in rubber compounding for about the same purposes as infusorial earth, and is also used in the manufacture of rubber type.

**GOLD OXIDE.**—As a matter of curiosity it may be noted that this is the most costly ingredient suggested for rubber compounding. It occurs in two forms—the protoxide, a dark green or bluish violet powder, and the teroxide, a brown powder. The use of the protoxide was patented by Ninck. For dental vulcanite it is doubtful if either form of the oxide could be used, even if the price were so low as to bring it within reach. Another formula calls for the mechanical admixture of gold leaf.

**GRAPHITE.**—See Plumbago.

**GYP SUM.**—See Calcium Sulphate.

**INFUSORIAL EARTH.**—It is known also as diatomaceous earth, Tripoli, fossil meal, mountain flour and kieselguhr. This is obtained usually from deposits at the bottom of inland waters, and consists of the minute siliceous remains of infusoria or microscopical animals. The largest deposits, in the form of a fine white or pinkish powder, are found in California, Nova Scotia, and in Germany. This earth is a wonderful non-conductor of heat, and, in connection with asbestos, is used in the manufacture of boiler coverings. It is used also in small proportions in various rubber compounds, where it increases both strength and resiliency, though if used in excess it makes a very hard compound. The best grades are wholly free from vegetable matter, are nearly pure silica, and perfectly indifferent to corrosive substances. Under the name of diatomaceous silica it is



used in a formula for elastic valve packing. This packing is described as practically indestructible in steam or water, oils, acids, etc. Specific gravity, 1.66 to 1.95.

IRON PYRITES.—A natural sulphuret of iron, about 5.20 specific gravity, commonly of a bright, brass-yellow color; a very plentiful mineral often mistaken for gold. It is used in the manufacture of sulphuric acid, while sulphur is also obtained from it by sublimation. It was used by Warne, Fanshaw, and others, in the manufacture of packings to resist a high degree of heat. The sulphur in iron pyrites has also been used in vulcanization. Warne, in one of his heat-resisting packings, patented the use of iron pyrites, and, in the compound that he gives as an example, leaves out the whole or a portion of the sulphur usually employed.

KAOLIN.—A white clay largely used in the manufacture of porcelain and to a degree in rubber compounds. It is a hydrated silicate of alumina. Specific gravity 2.20.

KERMES.—A brownish-red form of sulphide of antimony, artificially prepared by boiling in carbonate of soda. If left to itself the solution will partly deposit a very fine powder of kermes, while the clear solution may be further treated with a weak acid to obtain the remainder. Kermes will not vulcanize rubber without the addition of sulphur. Its specific gravity is about 4.5. Its composition is 28 per cent. sulphur and 72 per cent. antimony. It is rarely used in rubber compounding.

KIESELGUHR.—See Infusorial Earth.

LEAD ACETATE OR SUGAR OF LEAD.—A white poisonous powder soluble in water and alcohol. In its crystalline form it contains about 7 per cent. of water of crystallization, which is easily driven off at a temperature of, say, 80 degrees to 100 degrees F. Its specific gravity is: crystallized, 2.3; water-free, 2.5. Its use in semi-hard composition was patented by both Goodyear and Payen. India rubber dissolved in oil, to which has been added acetate of lead, is used to fill the pores of certain leathers so that the "filling" shall not come through. It is also used in certain varnishes in connection with gutta-percha.

LEAD CARBONATE.—See White Lead.

LEAD OXIDE.—See Minium and Litharge.

**LEAD OXYCHLORIDE.**—There are several oxychlorides of lead. Their specific gravity may be taken at 7.20. The substance once known as Turner's yellow and another known as Carsel yellow were both of this composition. More recently a white compound has been prepared, which, from its covering power, has been used largely as a paint. Tarpaulin compounds consisting of india rubber, coal tar, and pitch are treated with oxychloride of lead for surface drying, in lieu of vulcanization.

**LEAD PEROXIDE.**—The highest oxide of lead—a dark brown powder with a specific gravity of about 9.00. It is easily decomposed, and from this characteristic it has a strong oxidizing action. Exposed to sunlight or to heat, it yields oxygen and passes into the lower oxide known as red lead. Its oxidizing properties make it a questionable ingredient in compounding rubber, although certain formulas call for its presence.

**LEAD SULPHATE.**—A white powder of the specific gravity of 6.2, insoluble in water, but readily soluble in caustic alkalies. In Cooley's formula for artificial leather, which has gutta-percha for a base, it is used in connection with dextrine, magnesia, and cotton dust.

**LIME.**—The oxide of the metal calcium. It is commonly known in two states, viz.: quicklime, which is the pure oxide, and slaked lime, which is the hydrated oxide mixed with some carbonate. Quicklime is a white solid substance of specific gravity 3.2. It is not stable, taking up water and carbonic acid from the air and breaking down into a fine white powder, usually called air-slaked lime. Its power of absorbing water has caused it to be favorably used in drying operations, while the insoluble compounds it forms with various oils have led to its being considered as a drier, although this action is not properly to be called one of drying. Lime, air-slaked (specific gravity 2.40), is used in rubber work, where there may be a little moisture in a compound, which it readily neutralizes. It is also used in soft cements in connection with tallow and india rubber, but only where the rubber has been melted and the cement is of the non-drying variety. In compositions like that of Sorel's, lime is introduced to effect a combination between resin acids found in the resin and resin oil. Excess of lime in india rubber is injurious, because it renders the compound too dry, thus induc-

ing oxidation. When used in small quantities, aside from its effect upon moisture, it combines with free sulphur and modifies its continued action upon the rubber. It must be remembered, however, that lime diminishes the resiliency of india rubber, while it increases the hardness of both hard and soft rubber. It may be used in small quantities in insulated wire, and in a measure assists the insulating capacity of the rubber. Rubber also cures quicker when compounded with lime.

LITHARGE.—One of the oxides of the lead, known as the monoxide. When pure its specific gravity is 9.36. Commercial litharge often contains carbonic acid gas and water taken up from the air. These may be removed by strong heating. It has a peculiar property, the nature of which is yet a debated question, by virtue of which it renders oil more easily oxidized, or, as it is commonly called, rendered dry. There is no reason to suppose that this action is available with caoutchouc. The best litharge is made from pig lead, which is placed in a reverberatory furnace and exposed to a current of air, which burns it to an oxide. It has been noted in rubber factories that certain men seem sensitive to the effects of litharge, often developing symptoms of lead poisoning. Persons who show any symptoms should pay scrupulous attention to personal cleanliness. It is said that such persons have been cured by taking them out of the mixing room entirely, and putting them to work on vulcanizers, particularly where they open and handle the goods from the finished heat, the theory being that the sulphur fumes neutralize the effects of the lead. Possibly there is a grain of wisdom in this, for the old-fashioned treatment for lead poisoning was sulphur baths and the drinking of water acidulated with sulphuric acid or the acid sulphate of magnesia. Litharge is not only a valuable filler for rubber, but has the faculty of hastening vulcanization in a marked degree. In other words it is an accelerator. All dry heat goods depend upon it, and in mold work and general mechanical goods it is used whenever possible. Of course, it is generally available for dark or black effects only.

LITHARGRITE.—A substitute for litharge, made of a mixture of pulverized and calcined magnesia and oxide of lead.

LITHOPONE.—See Colors.

MAGNESIA.—A calcined white dry powder which, with water, forms a hard, compact mass like marble. Its specific gravity is 3.65. It is earthy in its nature, having no taste, but producing a sense of dryness in the mouth, owing to its absorption of moisture. It is frequently called calcined magnesia from the method of preparation by burning magnesia alba. Its use in rubber is to increase its toughness and resiliency, which it does to a marked degree when used in moderation. Magnesia is also used in the production of compounds like balenite, its use in hard rubber compounds being to increase resiliency as well as hardness. A very small quantity of it is also used in compounds for insulated wire, where it is said to increase the insulating qualities of rubber. Carbonate of magnesia occurs native in the mineral magnesite and, in connection with carbonate of lime, as dolomite.

There exist two kinds of calcined magnesia: the *heavy* and the *light* calcined. Heavy calcined magnesia is produced by calcining heavy carbonate of magnesia, which carbonate is won by precipitation of hot magnesia solutions by hot solutions of soda. The light calcined magnesia is produced by calcining the light carbonate of magnesia, and this light carbonate is the precipitation product of magnesia solution together with soda solutions, both carefully cooled. The difference between kinds of calcined magnesia concerns only the structure, so that light calcined magnesia in a dry state seems to have a very big volume, but if the included air is expelled, the big volume cannot have the expected effect, if light calcined magnesia is kneaded together with india rubber on the mixing rollers. The vulcanization of india rubber can easily be accelerated by addition of calcined magnesia. Such an addition is often necessary with soft rubbers in open steam-cured compounds. Rubbers with a high amount of resins, such as Guayule, Cameroons, Assam, Borneo, etc., usually give better results if compounded with appropriate additions of calcined magnesia.

MANGANESE PEROXIDE.—Another name for black oxide of manganese, which is a black powder having a specific gravity of 4.8. It is not readily acted on in ordinary ways, being unchanged by heat short of bright red. It is insoluble in the

ordinary hydrocarbon solvents. Solvent naphtha was treated with peroxide of manganese by Humphry to free it from water.

Oxides of manganese have a destructive effect on rubber, and blacks that contain this, as they sometimes do, are to be avoided. Manganese is used in connection with pitch, turpentine, and gutta-percha for making Brandt's cement.

**MARBLE FLOUR.**—This is the finely ground chips of white marble, composed almost wholly of carbonate of lime. It is a heavy inert powder used in rubber compounding as a substitute for barytes. It has also been used to some extent in hard rubber, and in the manufacture of hones. Specific gravity 2.65 to 2.75.

**MASSICOT.**—A monoxide of lead (lighter yellow than litharge). Specific gravity 7.90. A higher degree of oxidation turns this into a product called minium or red lead. It is often used in rubber compounds, acting practically like litharge.

**MICA** is the name given to a group of complex silicates containing aluminum and potassium, generally with magnesium, but rarely with lime. Their specific gravity ranges from 2.8 to 3.2, while their color varies greatly. Ground mica is simply one or other of these micas reduced to powder. It is used in rubber compounding chiefly for insulating purposes. It is handled as a cement, compounded with rubber, and cut with benzine, or may be mixed dry on the grinder. It is also used in fireproof coverings in connection with rubber, and it is said that for a semi-hard result that is to come in contact with hot water, rubber and mica form the best compound. Mica in a state of a very fine powder is also known as "cat's gold" or "cat's silver."

**MINERAL WOOL.**—Produced by sending blasts of steam through molten slag, which reduces the fluid metal to a fiber similar to the fused glass that is spun into glass silk. Natural mineral wool, such as is found in the Hawaiian Islands, is very brittle, but the artificial has considerable toughness. It is also known as slag wool, or silicate cotton. It appears in light fleecy masses, and at a distance looks like fine cotton batting. It is very cheap, but is easily affected by weak acids, and should be kept away from a moist atmosphere. It has not been largely used in rubber work as yet, but Lascelles-Scott strongly advises its use, giving as reasons its cheapness and its physical fitness. The sulphides present in it also assist in vulcanization.



MINIUM.—See Red Lead.

MOUNTAIN FLOUR.—See Infusorial Earth.

ORANGE MINERAL.—A red lead made from carbonate of lead, while red lead is made from litharge. As a general rule, it contains some lead carbonate. It differs from red lead in color, in that it is more orange red, and more brilliant. The reason for this difference is that it is less crystalline, its particles being much finer than those of red lead. The pigment is also more bulky and much smoother. It is used in finer grades of dark rubber, to assist the cure and impart resiliency. Its specific gravity is 6.95.

OSSEIN.—A light powder made from specially treated bone. Said not to be affected by acids. Is not affected by heat and is not hygroscopic. Preparation patented in England by J. F. Hunter.

PAGODITE.—A mineral resembling steatite or soapstone. Its name comes from its having been used in the East as a material for carving miniature temples or pagodas from, as it is soft enough to be cut with a knife. Its specific gravity is the same as that of soapstone (about 2.70), and its color greenish white. See Agalmatolite.

PARIS WHITE.—This has exactly the same composition as whiting, but is a much harder and more compact form of English chalk, and therefore has greater density. Spanish white is a coarser variety of the same material. Its uses are practically the same as those of whiting. Specific gravity 2.70. See Whiting.

PERMANENT WHITE.—See Blanc Fixe.

PETRIFITE.—A white powder composed of two inexpensive but secret substances. When mixed with water it solidifies quickly, and is an excellent binding substance. Mixed with marble dust, it is sometimes melted and cast upon glass or other smooth surfaces, and makes an excellent table-top in place of the zinc tables used in many rubber factories. As it is perfectly impervious to ordinary solvents, neither cement nor india rubber sticks to it. It is manufactured in England.

PHOSPHORUS.—A non-metallic element or metalloid, although in its combining relation it is more closely connected with arsenic and antimony than with any members of the sul-

phur group. It is found ordinarily in two states—the ordinary phosphorus and the red variety. Ordinarily phosphorus is an almost colorless or faintly yellow substance, somewhat resembling wax, and giving off a disagreeable odor. It fuses at 111.5 degrees F. into a colorless fluid. Heated in the air to about 140 degrees F., it catches fire and burns with a bright white flame. It dissolves freely in benzol, bisulphide of carbon, and in many oils. Red phosphorus is an amorphous powder of a deep red color, with no odor, and may be heated to nearly 500 degrees F. without fusing. Its specific gravity is 2.10. It does not take fire when rubbed, undergoes no change on exposure to the air at ordinary temperatures, and is far less inflammable than ordinary phosphorus. It is insoluble in solvents of the ordinary phosphorus, and is not poisonous. Mulholland made an insulated wire compound from shellac and india rubber in solution, combined with one to two per cent. of phosphorus, which he cured with chloride of sulphur. As cold-cure gums are of little value as insulators his invention is of doubtful value. He also made a preparation of india rubber, resin and tallow, and shoddy, to be applied in a fluid state where gas came in contact with rubber, adding phosphorus after his solution was finished, to prevent decomposition of the rubber. Duvivier also treated gutta-percha with sulphide of phosphorus, claiming that he got an elastic result, but allowing that his compound was damaged by acid vapors, to neutralize which action he mixed carbonate of soda with it. An anti-fouling preparation of English origin was also made of gutta-percha, turpentine, and a little phosphorus.

PIPE CLAY.—A peculiar kind of clay containing neither iron, sand, nor carbonate of lime. It is beautifully white, retaining its whiteness when burnt. Its specific gravity is 2 to 2.5. It was used by Mayall in combination with gutta-percha, india rubber, zinc, shellac, and resin for insulating tape, and by Austin G. Day to absorb gases during vulcanization.

PLASTER OF PARIS.—This is prepared by calcining gypsum or sulphate of lime. Its properties of hardening when made into a paste with water are well known. It is used sometimes instead of lime in compounding and also for making trial molds for rubber work. It was used in old-fashioned dry heat com-

pounds to prevent blistering. Specific gravity 3.2. See Anhydrite.

**PLUMBAGINE.**—A dark-colored pigment manufactured in England and sold to rubber manufacturers for the production of valves. By its use the rubber is vulcanized and goods made which are said to resist successfully the action of cheap lubricants. One pound of plumbagine is used to two pounds of rubber.

**PLUMBAGO.**—This sometimes is called black lead, though having no relation to lead; it is also called graphite. Its specific gravity is 2.1 to 2.2. Its color is black and shiny. It consists chiefly of carbon, but contains more or less alumina, silica, lime, iron, etc., varying from 1 to 47 per cent., but not chemically combined. Black lead is a perfect conductor of electricity. It is more incombustible than most ingredients used in rubber compounding, and is capable of withstanding great heat. It is used in the rubber industry, chiefly in the manufacture of what are known as graphite or plumbago packings. It is a wholly inert substance, safe to use in connection with any compounds, and is not affected by heat or acids, alkalies, or corrosive substances. It is useful also in certain polishing compositions made with india rubber as a base. Almost all German asbestos cements contain a proportion of finely powdered graphite.

**PORTLAND CEMENT** was first obtained by burning the mud found at the mouths of several large rivers in Europe with a proportion of clay and lime. Its composition is somewhat complex, containing: lime 55 to 63 per cent, silicic acid 23 to 26 per cent., alumina 5 to 9 per cent., and oxide of iron 2 to 6 per cent., together with magnesia, potash, soda, sulphate of lime, clay, or sand in various small proportions, according to the mode of manufacture. Its specific gravity is 3.00-3.10. Its value as a cement depends upon the interaction of the lime and the silicic acid. In compounding it would have no chemical effects upon rubber, but might of itself become much hardened and thus cause mechanical injury to goods in which it has been introduced. As it occurs commercially, it is a gritty powder of a gray-brown or yellow-brown color. Its only use as far as known in rubber is where it is mixed with tar oil and waste rubber to joint pipes containing fluids.

**POWDERED COAL.**—Coal consists chiefly of carbon, and is universally regarded as being of vegetable origin. Various coals differ widely in their composition and characters, running from the softest kinds of earths to compact and solid bodies like parrot coal, which is so compact and solid that it has been made into boxes, inkstands, and other articles which resemble jet. The average specimen of coal analysis is: carbon 82.6, hydrogen 5.6, oxygen 11.8. Some curious compounds of india rubber and coal have been formed. One, for instance, was a mixture in which two pounds of waste india rubber in a cheap solvent was mixed with nearly a ton of powdered coal (specific gravity 1.25-1.75), which contained some clay and peat, the use being for an artificial fuel; another use was in the production of hard rubber.

**PUMICE.**—A light, porous, ashy stone, specific gravity 2.20-2.50, the product of volcanic action, its structure being that of a mass of porous glass. Its composition is a mixture of silicates of aluminum, magnesia, calcium, iron, potassium, and sodium, varying with the particular lava whence it had its origin. Its action on india rubber will be quite inappreciable, chemically speaking, but its mechanical action will be that of a sharp cutting powder. Ground fine, it is used in the manufacture of erasive rubber, and is also used compounded with the rubber in the manufacture of hones. Recent patents call for its use in certain semi-hard compounds, its presence being said greatly to increase their toughness. Mixed with lard oil to a thick paste, this has been used for polishing india rubber.

It is particularly valuable for use in the dry-heat cure of such articles as water-bags and bottles. The goods filled, bedded and covered with fine pumice powder are evenly cured without discoloration or change of color. In this respect pumice is superior to talc for the purpose, and the goods are more easily washed clean.

**PUZZOLANA.**—A porous lava found near Naples, used chiefly, when mixed with ordinary lime, in forming hydraulic cement. Compounded with marine glue, it is used as a varnish for preserving metallic articles from corrosion.

**RED CHALK.**—Artificially deposited chalk colored by any suitable pigment—usually one of the red oxides of iron. See Chalk.

**RED LEAD.**—An oxide of the metal, which is also known as minium. Prepared from pure massicot or from white lead. Its specific gravity is 8.6 to 9.1. A scarlet crystalline granular powder, of rather strong coloring powers. As a colorant in rubber work it would be unavailable, since the sulphur necessary to vulcanize would render it more or less black, owing to the formation of sulphide of lead. It is sometimes used, however, in place of litharge. It is also used in "hot" cements of gutta-percha and for varnishes such as those made of india rubber, linseed oil, etc., for covering the backs of mirrors. See Minium, Massicot, and Orange Mineral.

**ROTTEN STONE.**—Usually considered to be the residuum of naturally decomposed impure limestone, and varying in composition with its sources. Specific gravity 1.98. That from Derbyshire, England, shows much alumina; other sorts have more silica. The name is sometimes incorrectly given to "Tripoli," which is a species of infusorial earth. It can have no particular action on rubber, as it is very inert, but it is used in certain packings, and was also used by Warne in insulated wire compounds.

**SELENIUM.**—A non-metallic element or metalloid of a dark-brown color, analogous to sulphur. Specific gravity 4.80. It has no smell and is a non-conductor of electricity. It occurs rarely in nature, being found chiefly as a selenide in combination with lead, silver, copper, or iron. It is the basis of an unused process for vulcanizing india rubber.

**SILEX.**—Pure silica. See Flint.

**SILICA.**—The oxide of the metal silicon, familiar in the forms of flint, quartz, etc. Its specific gravity is 2.6. It is without action on india rubber, except mechanically speaking. It is used in Chapman's vulcanite enameling solution, made of india rubber, sulphur and silica. See Flint.

**SILICATE COTTON.**—See Mineral Wool.

**SLAG WOOL.**—See Mineral Wool.

**SLAKED LIME.**—See Lime.

**SLATE.**—A soft, laminated, argillaceous material, chiefly aluminous in composition, and allied to the clays. Finely ground, it makes a good semi-hard valve of a blue-gray shade. It has been also used in general rubber compounding. Specific gravity 2.70.



**SOAPSTONE.**—A silicate of magnesia, combined with more or less alumina and water. It is really a massive form of talc. In color it is white, reddish, or yellow, is soft and greasy to the touch, is easily cut, but is hard to break. Its specific gravity is 2.26. It is used often in the place of French talc, for keeping rubber surfaces from sticking together during vulcanization, and also for burying dark colored goods and holding them in shape while they are being cured. Used as an adulterant for rubber, it makes an excellent semi-hard compound for valves. It is also used as a basis compound in the manufacture of insulated wire. See Talc.

**STARCH.**—A vegetable substance allied closely to cellulose. It occurs in regular lumps composed of granules which have a definite character, according to the variety of the plant from which they were derived. When dry its specific gravity is 1.53. Commercial starch contains usually about 18 per cent. of water and, if kept in a damp place, will absorb 33 per cent. of water. It was much used formerly on solarized work. Torrefied starch is obtained by roasting the common form, and is used in artificial leather compounds.

**SUBLIMED LEAD.**—A white lead known as sublimed lead is used very largely in rubber manufacture. It is a fine white amorphous powder and imparts a decided toughness to rubber compounds. It acts both as a filler and chemically. Its peculiar velvety fineness makes it mix intimately with the rubber, and gives a very fine finish, showing no shiny crystals on the surface. The oxide of lead in the sublimed lead will also bind free sulphur in the rubber. The amorphous state of the sublimed lead makes the action of the lead oxide in this much more effective than the action of litharge, and the result is a very smooth, lively, jet-black rubber. Specific gravity 6.20.

**SUGAR OF LEAD.**—See Lead Acetate.

**TALC OR FRENCH TALC** is a mineral allied to mica. It is composed entirely of silica and magnesia, in the proportions of 67 to 73 of silica, 30 to 35 of magnesia, and 2 to 6 of water. Specific gravity 2.70. Its colors are silvery white, greenish white, and green. Talc slate is more like steatite and is used for similar purposes. French talc is used very largely in rubber

factories in all lines of work for preventing surfaces from sticking together, during either manipulation or vulcanization. It is also used commonly for dusting molds to prevent the gum from sticking to the metal and extensively to bury white goods and keep them in shape during vulcanization. It is used sometimes in compounding, but any great amount of it produces a stony effect. It makes, however, an excellent semi-hard packing. It is used further in compounds for soft polishing, with india rubber as a binding material.

**TALITE.**—A white earthy material used in general rubber compounding. It is allied to diatomaceous earth, presumably, and has the same usage. Its analysis shows: Moisture 5.59, silica 83.9, sesquioxide of iron 1.2, alumina 2.8, oxide of manganese trace, potash trace, combined water and organic matter (by ignition) 6.47, loss and undetermined 0.04—total 100.

**TIN OXIDE.**—The form most frequently used in the arts is the dioxide. This is a white water-free powder, of the specific gravity of 6.7, insoluble in acids and such solvents as naphtha, petroleum, etc. It is infusible, except at a very high temperature, tasteless and inodorous. French oxide of tin is a carefully prepared and purified form of the dioxide. It is rarely used in rubber work, although Newton recommends it for a basic ingredient in rubber type. The other oxides of tin are at present merely of chemical interest.

**TRIPOLI.**—See Infusorial Earth and Rotten Stone.

**TYRE-LITH.**—A trade designation for colloidal barium sulphate. See Blanc Fixe.

**WHEAT FLOUR** is used in making matrices for rubber stamp work, and sometimes as a compounding material in india rubber, though this is not to be advised, as the flour is apt to sour. A standard low grade of wheat flour known as "red dog" is particularly suited to the purpose of dusting the skim coating of wool linings, because, owing to its peculiar texture, it is easily removable by a wash of thin cement in the making-up process and does not impair the adhesion to another rubber surface.

A large and important use for it has been in the dusting of black goods, such as rubber coats, so as to keep them from sticking together, should they accidentally touch during the dry heat

of vulcanization. Wheat flour is preferable to almost anything else, for the reason that it washes off after vulcanization, without leaving any trace in color or stain. It is used on the goods known as "dull finished."

**WHITE LEAD.**—This is a mixture of hydrated oxide and carbonate of lead and is a heavy white powder. It is unstable in color, however, as sulphur compounds, especially in the gaseous forms, easily attack it and blacken it by reason of the formation of sulphide of lead. Its specific gravity is 6.46. Sometimes it is adulterated with lead sulphate, chalk, carbonate, or sulphate of baryta, or pipe clay. The simplest test for the purity of white lead is to heat it in a thin glass vessel with some very dilute pure nitric acid; if pure it will dissolve completely. If chalk be present it also will pass into the solution, in which it may be detected by the addition of caustic potash, throwing it down as a white cloud. The best white lead is made by the old-fashioned Dutch process, which consists of packing the metallic lead, cast in the form of buckles to present a large surface for corrosion, in covered earthen pots, in the bottom of which is placed acetic acid. The pots, thus prepared, are stacked and buried in a mass of spent tan bark to conserve the heat caused by the reaction of the volatile acid on the metal. The original "triple compound," patented by Goodyear, consisted of india rubber, sulphur and white lead.

**WHITING OR CHALK,** as it is often called, is carbonate of lime. It is a white earthy material of the specific gravity of 2.7 to 2.9. It is made from English chalk, which is crushed, floated, and run through a filtering process, and dried in cakes made in varying degrees of fineness by a system of dry grinding and bolting. Where whiting is kiln-dried hastily, or under extreme heat, it is apt to become calcined, which gives it a hard, gritty feeling. Air-dried whiting is considered the best. Whiting is in reality a purified form of carbonate of calcium, of a very soft or flocculent quality. The finest grades are known as "gilders'" and "extra gilders'." It is used more generally in rubber compounding than any other material, except sulphur. Used moderately, it increases the resiliency of rubber, but adds to the hardness. It does not, however, produce the stony effect

that many ingredients give. The molds used in rubber-stamp making are composed of whiting, wheat flour, glue, and carbolic acid. Whiting is liable to absorb considerable quantities of water from the air. It is customary in many mills, therefore, to keep it in large bins that not only are covered but have steam pipes in the lower portions to drive out any moisture from the material.

WITHERITE.—See Carbonate of Barium.

ZINC OXIDE.—See Colors.

ZINC SULPHATE OR WHITE VITRIOL.—The crystals contain about 44 per cent. water of crystallization. Specific gravity 2.03.

ZINC SULPHIDE.—See Colors.

#### UNUSUAL INGREDIENTS IN DRY MIXING.

It is not strictly accurate, perhaps, to say that it is unusual for fibers to be incorporated in rubber mixtures, for stocks made from unvulcanized rubber clippings have been used for years. Inner soles for rubber footwear and mats, and molded articles have long been made of stocks of this kind, the fibers being cotton (as cotton linters) and wool, chiefly. Where wool was present there was oftentimes danger of blistering from the oil in the fiber, but this was easily gotten over by special compounding. In addition to the fibers already noted, silk, flax, jute and hemp—in fact, almost all of those in ordinary use—have been utilized, being added to the compounds to give toughness to them. The goods in which they are usually put are packings, gaskets, artificial leather, tire treads, shoe soles, and other wearing surfaces.

A fiber that has attracted considerable attention for this work, and one for which a number of patents have been granted, is coconut fiber, which is recommended for packings. Certain kinds of moss have also been used, as have sponge cuttings, peat, and wood pulp. This last-named material has been used both in packings and in insulated wire compounds. It is also the basis of a curious artificial rubber that appeared several years ago, under the name of maltha, but is not to be confused with the product that has become almost universally known by that name.

Sawdust of all kinds has also been incorporated in rubber, and was formerly used in making sponge rubber, until better

compounds were discovered. Those who use vegetable fibers prefer them unbleached rather than bleached, and very often treat them to remove resins that may be present. A few of the many other vegetable substances that have been used are sugar and sugar charcoal and seaweed.

Animal substances are also valuable, as for instance, animal charcoal, whalebone, which is specified in some of the Woodite patents, fur, tan-hair, leather fiber, currier's skivings, which are used in artificial leather, the white of eggs, glue, etc.

Under the head of earthy and metallic ingredients, almost anything can be used, although some metals have a bad effect on rubber, notably copper and manganese. The unusual earthy matters are powdered fossil iron-stone, Wisconsin mineral, coke ashes, Stourbridge clay, powdered granite, salt, powdered lithographic stones, powdered oyster shells, powdered schist; and in metals, steel, and all other common metal borings, filings, and turnings. These latter have been incorporated in packings as a rule. One packing in particular, which has had a world-wide reputation, was heavily compounded with brass filings.

DEODORIZATION OF RUBBER, and the neutralization either of the smell of the rubber or its solvent, has brought out also a curious line of ingredients. Musk, for example, has been used to disguise the earthy odor of gutta-percha. Alcoholic infusions of sage-tea, lavender, and verbenas have been used in fine goods, while in powdered form, ginger root, birch, orris root, sassafras, marshmallow root, sandal wood, and other sweet-smelling ingredients have been incorporated. The leaf of the mint has also been mingled with copperas and placed in dry heaters, while a more expensive process was that pursued by Hill, who passed a current of hot air over perfumes and into the heaters. It must not be imagined that the ideas expressed in the foregoing are unworthy of the consideration of those who make ordinary cheap mechanical goods, for certain of these ingredients are used today in mechanical mixtures to overcome the odors of African rubbers. Essential oils and gums are also used for the same purposes, the descriptions of which will be found under their proper departments.



Medical science has also added its list of ingredients to rubber compounding, chiefly in the line of adhesive plasters, where ingredients like dry mustard, menthol, capsicum, belladonna and a great variety of other medicaments are incorporated with the rubber.

## CHAPTER VII.

### SUBSTITUTES FOR INDIA RUBBER, NATURAL AND ARTIFICIAL.

RUBBER SUBSTITUTES, as a rule, are made from oxidized oils. Those used most generally are made from linseed, rapeseed, cottonseed, mustard, peanut, or corn oils, acted on either by chloride of sulphur or by sulphur boiled with the oil at a high temperature. Substitutes have been known over fifty years, and have been made the subjects of many patents, but only within the last twenty-five years have they come into general use. The fact that Europeans were unable at first to get the results with reclaimed rubber that were secured in the United States, led them to go further in their experiments with oxidized oils and to exploit their uses more thoroughly. The substitutes on the market today are, as a rule, white, brown, and black. They are often of the same specific gravity as pure india rubber, so that their presence cannot be detected in rubber compounds by specific gravity tests. Substitutes of this type are easily analyzed and the results of such analyses are of value to rubber manufacturers. The table on the next page, containing analyses of typical substitutes, is adapted from Dr. Robert Henriques.\*

It would be a mistake to suppose that rubber substitutes are of no value, for they possess certain very distinct advantages not found in simple mineral adulterants nor possessed by the bituminous products now in use. Their value, of course, is where they cheapen stock without seriously injuring its durability or changing its texture. Where substitutes are compounded with rubber they are used in small quantities, sometimes only 5 per cent. being added, and rarely is more than 25 per cent. to be found in good compound.

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\**"Journal of the Society of Chemical Industry,"* 1904, page 47.

## ANALYSES OF OIL SUBSTITUTES

OILS VULCANIZED WITH $S_2Cl_2$	Sulphur	Chlorine	Water	Residue on Ignition	Fatty Acids	Iodine Value	Acetyl Value	FATTY ACIDS		
								Sulphur	Chlorine	Iodine Value
<i>Substitute from:</i>	<i>Pr. Ct.</i>	<i>Pr. Ct.</i>	<i>Pr. Ct.</i>	<i>Pr. Ct.</i>	<i>Pr. Ct.</i>	<i>Pr. Ct.</i>	<i>Pr. Ct.</i>	<i>Pr. Ct.</i>	<i>Pr. Ct.</i>	<i>Pr. Ct.</i>
Linseed oil (raw oil) .....	9.34	8.84	3.02	.....	79.6	56.3	21.0	9.88	Trace	160.3
Linseed oil (blown oil) .....	4.78	4.85	0.85	.....	81.67	52.6	19.6	4.06	0.60	{ 141.2 121.0 }
Rape oil (commercial oil) .....	8.28	7.62	.....	.....	86.89	32.5	31.0	8.34	Trace	101.5
Rape oil (blown oil) .....	6.59	5.95	.....	.....	87.95	26.9	.....	6.54	Trace	102.8
Poppyseed oil (blown oil) .....	7.68	7.44	.....	.....	74.90	33.6	.....	8.32	.....	133.3
Cottonseed oil (blown oil) .....	6.23	5.36	.....	.....	.....	30.3	51.3	6.44	Trace	91.5
Castor oil (with minimum $S_2Cl_2$ ) ..	4.82	6.70	.....	.....	85.35	35.2	.....	5.32	Trace	{ 136.2 147.4 }
Castor oil (with maximum $S_2Cl_2$ ) ..	10.60	8.95	.....	.....	.....	21.9	105.6	.....	0.26	{ 152.1 105.6 }
<i>Commercial products:</i>										
White substitute No. 1 .....	6.4	5.0	0.85	0.8	90.45	30.9	.....	6.12	0.83	91.3
White substitute No. 2 .....	6.17	5.86	1.0	5.51	73.58	31.0	.....	6.45	0.43	91.2
White substitute No. 3 .....	8.25	8.88	.....	.....	.....	32.6	.....	8.15	.....	102.3
Brown substitute No. 1 .....	15.48	0.7	.....	.....	.....	42.0	.....	14.14	.....	129.0
Brown substitute No. 2 .....	17.71	0.36	.....	.....	.....	42.0	.....	15.20	.....	125.6

The list in the accompanying table has been made quite comprehensive, not because all the substitutes described are deemed valuable, but rather to give a broad view of the subject. It will be noticed that many of these gums are far out of the line of sulphurized oil experiments. Resins, glues, asphalt, cellulose, seaweed, bastard rubbers, animal substances, etc., have all been called upon and some of the treatments have been as original as the ingredients are unusual. To the end that the perfect substitute may be found, and with the fullest appreciation that anything which suggests new experiments has its value to the manufacturer, many that otherwise would be ignored are given here.

**ADAMANTA.**—A substitute for india rubber, made from linseed oil, sulphur, lime, and resin. It is a thick, black, gummy mass, with an odor similar to that of most of the sulphur oil substitutes, and showing a bright cleavage. It was at one time used largely in France and Germany, and introduced to some extent into the United States. Its chief use was in cheap mechanical rubber goods, and for insulation.

**ADHESOR.**—A sticky substitute used to a certain extent in frictions.

**ALGIN GUM.**—A gluey, leathery substance, manufactured from seawood. It is insoluble in cold water, alcohol, ether, and glycerine, and combines readily with alkaline and metallic bases to form substances, many of which are soluble. Algin can be used for waterproofing compounds, as it combines easily with rubber, shellac, and other gums. With many metallic bases it forms insoluble compounds as tough as horn or as pliable as gutta-percha. It is an English product.

**AMBER-RESIN SUBSTITUTE.**—An English patented substitute made of amber-resin dissolved in castor oil, heated with a little sulphur. Is treated with ozonized air after cooling. The mass then treated with chloride of sulphur in the presence of a solvent, calcium carbonate being also added.

**A. R. D. GUM.**—So called because it is used as an anti-dry-rot compound. It is manufactured of 112 parts glue, 56 parts resin, 10 parts boiled linseed, and 35 parts water. In some cases it has also been mixed with india rubber in general compounding. Patented by J. F. Ebner, London, England.

**ARTIFICIAL ELATERITE.**—Made from liquid bitumen by incorporating with it vegetable oils, such as cottonseed oil, palm oil, rapeseed oil, etc. The product is treated with the aid of heat and pressure, with chloride of sulphur, saltpeter, and sulphur, which produces an oxidization of the fatty substances. The result is an elastic rubber-like or leathery mass, which is soft, spongy, and gluey. This gum is said to be far more elastic than the best samples of mineral rubber, and is useful for waterproofing and insulation. Patented by W. Brierly, in England.

**ARTIFICIAL GUTTA-PERCHA.**—A French compound made of 50 parts copal, 15 parts sulphur, 30 parts turpentine, and 60 parts petroleum. While mixing the heat reaches 100 degrees C.; it is then cooled to 35 degrees C. Then there is added a solution of 3 parts casein, in weak ammonia, and a little methylene, and reheated to 120 degrees C. It is then boiled with a 15 or 20 per cent. solution of tannin, and 15 parts ammonia. After several hours' boiling it is washed and cooled.

**ASBESTONIT.**—An asbestos product manufactured in England under a secret process, for use as steam or hot-water packing.

**ASTRICTUM.**—A compound to be used in damp places, consisting of pulped cotton 15 pounds, pitch 25 pounds, asphalt 20 pounds, ground granite rock 20 pounds, bitumen 5 pounds, resin 10 pounds, coal tar 12 pounds, and mastic 5 pounds.

**BELLEDDIN'S PROCESS FOR LEATHER IMPREGNATION.**—Hides are treated in alkaline solutions and immersed in a bath of rubber solution.

**BORCHERDT'S** compound for dolls' heads consists of 5 pounds glue, 10 pounds sugar,  $2\frac{1}{2}$  pounds glycerine, 3 pounds Perry's white.

**BLACK GERMAN SUBSTITUTE.**—Made of boiled linseed oil and sulphur, together with resinate of lime. This gum is similar to adamanta, and has been practically driven out of the market by lighter substitutes.

**BLANDITE.**—An artificial india rubber invented by Dr. A. L. Blandy, of London. It is fairly elastic, stretching to about twice its length, and returning readily. It is very pliable and



does not show signs of cracking when bent. It is vulcanized like ordinary rubber, and can be molded into any form desired. Coated on cloth, it strongly resembles leather. It is waterproof, and is used for gas tubing, mats, etc. In its crude form, it is a liquid mass resembling molasses. Dr. Blandy's patent describes the compound as made preferably of linseed oil which has been reduced by oxidation; then 10 per cent. of bisulphide of carbon to which has been added 10 per cent. of chloride of sulphur, is mingled with the oil, and the mixture brought by gentle heating to the desired consistency. Trinidad asphalt, cleansed and reduced to powder, is combined under the heat in the proportion of 3 parts to 1 of oil. Care must be taken to avoid fire in heating. These proportions are gradually brought, by heat and stirring, to a liquid or thin state, and when in this condition it must be poured upon a wet, cold surface, and thus cast into sheets, convenient for subsequent mixings.

CAOUTCHENE.—A French substitute consisting of 100 parts sunflowerseed oil, 25 parts chloride of sulphur, and exposed to air ten days, when it becomes yellow and elastic. To this is added matesite, a Madagascar gum, and then isoprene is added.

CAOUTCHITE.—Vulcanized rubber exposed to heat (250 degrees F.) for several days and devulcanized and recovered by this means alone.

CARROL GUM.—A well-known sulphur oil substitute used in the United States. In smell it has all of the characteristics of the sulphurized oil products. It is produced usually in granular form, and is very black.

CEREAL RUBBER.—Wheat treated with ptyalin. The invention of William Threnfall Carr, of England. It is a gluey product which, after it comes from the so-called vulcanizing press, is said to be both plastic and waterproof.

CHICLE SUBSTITUTE.—A specially prepared cottonseed oil substitute. Said to be very largely used by manufacturers of chewing gum. See Gum-carbo.

CHRISTIA GUM.—An English substitute for gutta-percha or india rubber, used as a surgical dressing. It is said to be composed of hemp fibers, so treated as to be impervious to both

alcohol and water. Dieterich analyzed a sample of the product, and said that the fibers were sulphite wood pulp, and that the coating was made from chrome gelatine treated with glycerine, or the well-known compound of glue, glycerine, and bichromate of potassium.

CON-CURRENT RUBBER.—Invention of Julius Nagel, of New York. A secret compound, the basis of which is linseed oil and resins.

CORKALINE is made of glue, glycerine, ground cork, and chromic and tannic acids. It is of English derivation and is used as a substitute in mat work.

CORK LEATHER.—A French invention composed of thin sheets of cork, covered on both sides with an extremely thin india rubber skin, and of a textile fabric outside. It is very light, is a good insulator against heat, and is waterproof.

CORN OIL SUBSTITUTE.—A sulphurized oil substitute similar to that made from oxidized linseed or rapeseed oils, manufactured from corn or maize oil. It is the cheapest oil substitute that has yet been put on the market. It is made in two colors, brown and straw, and is used in large quantities in mechanical goods and in proofing. A good example of this type of substitute is that known on the market as "Kommoid."

DANKWERTH'S RUSSIAN SUBSTITUTE.—This is said to be a perfect substitute for both gutta-percha and india rubber, and is used for covering telegraph cables. High temperatures do not affect it. It is made of 1 part by weight of the mixture of equal parts of wood tar and coal tar oil, with 2 parts of hemp oil heated until the mass is of the right consistency. Then 1.3 by weight of boiled linseed oil is added. To this is added a little ozocerite and spermaceti. It is then heated again, and finally a little sulphur is added.

DERMATINE.—A well-known substitute for india rubber and leather, made of an artificial gutta-percha called "gum percha," 7 pounds; powdered waste rubber, 7 pounds; india rubber, 14 pounds; sulphide of antimony, 6 pounds; peroxide of iron, 2 pounds; flour of sulphur, 4 pounds 8 ounces; alum, 4 pounds 8 ounces; asbestos powder, 2 pounds; sulphuret of zinc, 3 pounds;

carbonate of magnesia, 7 pounds. A little change in this compound adapts it for machine belts. A variety of colors is gained by mixing in various pigments in place of sulphuret of antimony or peroxide of iron. The invention is patented by Maximilian Zingler, of London. It is claimed that dermatine will stand more wear than either leather or rubber, that it is absolutely unaffected by heat, cold, dryness, or moisture; and that it will stand perfectly the action of grease, oils, or acids. Adaptations of the formula given above permit it to be manufactured in molded forms. It is used for valves, packing, etc., and also for covering insulated wire.

DOEBRICH'S COMPOUND for dolls' heads consists of 1 pound glue,  $\frac{1}{2}$  pound glycerine,  $\frac{1}{2}$  pound sugar, and 1 tablespoonful pulverized flour, with a little albumen and coloring matter.

DURATE.—An artificial rubber compound said to be similar to dermatine.

EKERT'S HIGH PRESSURE COMPOSITION.—Consists of rubber, asbestos fiber, litharge and sulphur. To this base are added oxide of zinc, iron oxide, graphite, magnesium silicate and resin. It is patented.

ELASTEINE.—An elastic substance produced from solid and semi-solid copal resins and oleic acid, which entirely dissolves them. The product is soluble in spirits of turpentine and in oil. This solution of gums in oleic acid gives an opportunity to produce materials that have sometimes the elasticity and the consistency of india rubber. The inventor advises their use in insulating wire and in various kinds of proofing. It is of French origin, patented by M. Louis Riviere.

ELASTIC GLUE.—A mixture of dry glue and glycerine in equal parts, by weight. As little water should be used as possible in its manufacture. It is used for elastic figures, galvanoplastic molds, etc. It is not waterproof, nor will it stand a high degree of heat.

ELASTICITE.—Trade name for an American corn oil substitute.

ELASTITE.—A brown rubber substitute of German origin of the sulphur oil type.

**ENDURITE.**—The invention of John Stuart Campbell, of England. The basis of it is rubber and it is used in golf balls, belting, etc.

**EUPHORBIA RUBBER.**—J. G. Boles reduced Euphorbia gum to a fine powder and, after drying carefully at a low temperature, put it in solution and finally hardened it by mixing it with earthy matters and shellac.

**FAYOLLES' SUBSTITUTE.**—A French substitute for waterproofing, made as follows: 1 part sulphuric acid, 1 part glycerine,  $1\frac{1}{2}$  parts formalin, 1 part phenol.

**FENTON'S ARTIFICIAL INDIA RUBBER.**—Manufactured from linseed or similar oils, mixed with tar, pitch, or other pyroligneous products, the mixture being placed in a bath of diluted nitric acid, and allowed to remain until, by the action of the bath upon the compound, the whole is coagulated into a tough, elastic magna. The black "Fenton" contains as coloring matter a small quantity of plumbago or black carbonate of iron. The gum is patented by Ferrar Fenton, London, England. In his specification he modifies it by taking the artificial gum described, and placing it in a bath composed of a solution of sugar of lead, oxide of zinc, saltpeter, or some other form of nitrate, and, if high flexibility is desired, adds 5 to 10 per cent. to copal gum and nitric acid diluted with water. These solutions are used one at a time, the proportion being 5 per cent. of sugar of lead, or, for greater hardness, 5 to  $7\frac{1}{2}$  per cent. of saltpeter to the weight of the magna. Before vulcanizing, the substances are washed in an alkaline solution to remove acid. Fenton rubber is said to have been subjected to 320 degrees F. for fifteen minutes, the only result being to increase its elasticity.

**FIBRINE-CHRISTIA GUM** is manufactured just as Christia gum is, except that silk fibers are used in the place of hemp.

**FIG JUICE PROOFING.**—A French composition made up of fig juice, Brazilian tapioca, and pearl moss, together with vulcanized rubber. Used as a preservative and proofing compound.

**FIRMUS.**—An English rubber substitute presumably of the sulphurized oil order.

FRANKLIN SUBSTITUTE.—A mixture of coal tar and boracic acid dissolved in alcohol. Boiled and oxidized.

FRENCH GUTTA-PERCHA.—This gum is made by boiling the outer bark of the birch tree in water. The result is a fluid, which is very black, and which becomes compact and solid on cooling. It has been claimed that it possesses all of the good properties of gutta-percha, and that in addition it does not oxidize when exposed to the air. Its application for industrial purposes has been patented.

FROST RUBBER.—Another name for what is practically sponge rubber made from any ordinary unvulcanized rubber compound by the addition of a little alum or carbonate of ammonia.

GRAPE RUBBER.—A plaster produced from the skins and seeds of grapes from which wine has been extracted by pressure.

GRISCOM'S SUBSTITUTE.—A substitute composed of equal parts of animal fat, candle tar, and a residual product from petroleum, together with sulphur in proportions of from 2 to 8 per cent. of the mass.

GRONT AND MOORE'S REPAIR CEMENT.—A mixture of unvulcanized stamp rubber in benzine solution to which are added turpentine and collodion.

GUM-CARBO.—Substitute made from cottonseed oil. Used in general rubber compounding.

GUM FIBRINE is made of paper rags treated with liquid carbonic acid, mixed with resin, gum benzoin, and castor oil, dissolved in methylated alcohol. It is an English compound.

GUTTALINE.—A substitute for india rubber and gutta-percha, manufactured as follows: To Manila gum tempered with benzine is added 5 per cent. of Auvergne bitumen, also mixed with benzine. Then add 5 per cent. of resin oil, and allow 48 to 86 hours to pass between treatments. The product obtained is similar to india rubber. If it be too fluid, the addition of 4 per cent. of sulphur dissolved in bisulphide of carbon will act as a remedy.

GUTTA-PERCHA SUBSTITUTE.—Formula: 2 parts paraffin, 2 parts pitch,  $2\frac{1}{2}$  parts Chinese wood oil, 1.1 parts chloride of sulphur, 0.1 of sulphur. Heat to 100 degrees C. for one hour.



**HARMER'S SUBSTITUTE.**—Composed of 150 pounds waste rubber, 50 pounds Pontianak, 8 pounds African flake, 10 pounds substitute. Patented.

**HEVEENITE.**—Another name for heveenoid.

**HEVEENOID.**—This is claimed to be more insoluble, durable, and pliable than almost any other rubber composition. Soft heveenoid consists of india rubber 32 parts, camphor 32 parts, lime 1 part, and sulphur 8 parts. Hard heveenoid is made of india rubber 6 parts, camphor 4 parts, glycerine 1 part, and sulphur 16 parts. Heveenoid is the invention of Henry Gerner, of New York, and is patented in the United States and Europe. Kauri gum is also in certain heveenoid compositions. One special advantage claimed as to the use of camphor is that the chemical compound termed sulphide of camphor is produced, and therefore the rubber does not bloom.

**HYDROCARBON RUBBER.**—The invention of Eugene Turpin, of England. Made by heating a vegetable oil, oxidizing by air current, adding 25 per cent. by weight of resin, 25 per cent. powdered sulphur, 5 per cent. spirits of turpentine, and 1 to 2 per cent. carbon chloride.

**HYDROLAINE.**—One of the original waterproof fabrics made by means of india rubber dissolved in spirits of turpentine and spirits of wine in equal quantities, and deodorized by oil of wormwood.

**INDIA RUBBER LEATHER.**—A compound produced by Nelson Goodyear in which fibrous substances were mixed with india rubber to form a body, the surface of which resembles leather.

**INSULITE.**—A preparation made of wood or vegetable fiber, finely ground and desiccated, and saturated with a mixture consisting of melted asphalt, incorporated with substances of the resin type, with or without substances of the paraffin or anthracene types. The products resulting are used as substitutes for india rubber, particularly in insulation. Patented by Alfred H. Huth, London.

**IRESON'S PACKING COMPOUND** consists of a mixture of rubber, ultramarine blue, and silicate of magnesia.

**JACKSON'S COMPOUND FOR PRINTERS' ROLLERS.**—Sixteen pounds glue, 16 pounds glycerine, 1 pound borax, 1 pound japan.

JOHNSTONE'S NON-DRYING COMPOUND consists of gutta-percha, resin, and carnauba wax.

JONES'S SUBSTITUTE.—An English substitute made of treated pseudo gums. Marketed by the Rubber Substitutes Syndicate, Limited, of London.

JUNGBLUTH'S COMPOUND.—Calcium carbonate 75 per cent., Trinidad asphalt 20 per cent., selenite 5 per cent. In place of Trinidad asphalt, neutralite, an asphaltic material made in Berlin is sometimes used.

JUST'S ACID-PROOF COMPOSITION is composed of linseed oil, gutta-percha, sulphur, rosin, shellac, and asphaltum or pitch.

KAMPTULICON.—An india rubber compound for floor coverings. The simplest English formula is a vegetable fibrous material ground into a coarse powder, mixed with india rubber, and treated with a cheap solvent, such as coal tar or naphtha. Coloring matters are added, if desired. Another kamptulicon compound is: gutta-percha, cheap grade, 6 pounds; reclaimed rubber, 12 pounds; residuum from distilling palm oil, 6 pounds; ground cork, 4 pounds; ground chalk, 2 pounds; sulphur, 6 pounds; hair, 1 pound; oxide of zinc, 1 pound.

KELGUM.—A linseed oil preparation manufactured in the following way: First, boiling linseed oil in a nitric acid bath until it reaches a gum-like condition; second, subjecting the gum to a bath for the removal of the acid; third, cutting the gum in a solvent bath; fourth, disintegrating the gum with the solvent; fifth, grinding the disintegrated mass; sixth, boiling the material; seventh, subjecting the same to another boiling, and adding a drier. Used in proofing compounds. Invented by Henry Kellog, United States.

KERITE.—A compound of vegetable oils, coal tar, bitumen, and sulphur, to which are added sometimes a little camphor and various waxes. Occasionally sulphide of antimony is used in place of sulphur. Vegetable astringents such as tannin, the extract of oak bark, etc., are also used in small quantities to impart toughness. Kerite is the invention of Austin G. Day, and has been used largely for the manufacture of a covering for insulated wire. A later patent taken out by W. R. Brixey,

changes the original kerite compound somewhat. Cottonseed oil is eliminated and talc added. The later compound is as follows:

## KERITE.

Coal tar .....	25 pounds.
Asphalt .....	15 pounds.
Heat together to 350° F. for ½ hour; then add—	
Linseed oil .....	70 pounds.
Heat again to 350° F. for 7 hours; let stand over night; heat up to 240° F., and add—	
Sulphur .....	10 pounds.
Heat up to 320° F. in ½ hour and add—	
Sulphur .....	4 pounds.
Heat again to 300° F. and add—	
Talc .....	56 pounds.
Keep at same temperature ½ to ¾ hour, when vulcanization will have taken place, and the mixture can be poured into molds or allowed to cool in mass.	

KIRRRAGE COMPOUND.—A well-known English patented compound, which takes its name from the inventor. It comes in two forms. The first, to be used not over 200 degrees F., is composed of india rubber 12 pounds, gutta-percha 4 pounds, Stockholm tar 25 pounds, chalk 60 pounds, hemp 4 pounds, and sulphur 10 pounds. The same inventor also recommends the following, to withstand a great heat and pressure: india rubber 20 pounds, tar 25 pounds, coke, finely powdered, 25 pounds; Stourbridge clay 25 pounds, sulphur 10 pounds, fine emery 25 pounds, and steel filings 5 pounds.

KOMMOID.—See Corn Oil Substitute.

LEATHERINE is a compound that closely resembles derma-tine, and in fact a part of the first patent on that product. It is intended as a substitute for leather cloth and is made as follows: india rubber 28 pounds, substitute 10 pounds, sulphuret of antimony 13 pounds, peroxide of iron 4 pounds, sulphur 3 pounds, sulphuret of zinc 10 pounds, carbonate of magnesia 23 pounds, and sulphate baryta 8 pounds.

LEATHERUBBER COMPOUND.—Made of ground waste rubber, leather and reclaimed rubber. Manufactured largely in Australia.

LEONARD'S SUBSTITUTE.—Consists of a mixture of corn oil, castor oil, chloride of sulphur, naphtha, and oxide of magnesia.

LICONITE, produced in Holland, is described as a mixture of bitumen and various oils, without india rubber or gutta-

percha, elastic and tough, and is claimed to be unaffected by water, dilute acids, and alkalies, and neither flows nor cracks in ordinary temperatures.

LIMEITE.—A cement that is manufactured from melted india rubber, with the addition of 8 per cent. of tallow, with sufficient slaked lime to give it the consistency of soft paste. The addition of 20 per cent. vermilion causes the mass to harden immediately.

LINOXIN.—An insoluble oxy-compound produced by the oxidation of certain drying oils boiled in acetone or acetic acid, from which is produced an elastic mass similar to india rubber. Of French origin.

LUFT'S CELLULOID RUBBER.—By boiling equal parts of phenol and 50 per cent. formaldehyde with sulphuric acid and to the washed and dried product adding india rubber, a compound is formed that, boiled in alkaline solutions, is transparent and similar to celluloid.

LUGO.—A rubber substitute patented in England, made by heating a mixture of oxidized oil and rubber to a temperature at which the rubber dissolves. Potassium permanganate is added, and the whole heated to 360-400 degrees F. Finely divided waste rubber is added, the mass being stirred and the temperature maintained. To obtain a harder product sulphur may be added.

LUGO RUBBER.—An artificial oxidized oil substitute that once had a large sale. It was black, of about the same specific gravity as india rubber, and made, in connection with rubber, excellent mold work.

MADANITE.—A binding material for smooth surfaces, such as air-pumps, etc., made of 2 parts by weight of vaseline, and 1 part india rubber, melted. This mixture may be left for years without perceptible alteration. A low-grade gum used in the same way in connection with vaseline makes an excellent insulating tape, and has also been used as a friction gum.

MAPONITE.—A substitute for india rubber and gutta-percha, claimed to be capable of use in the manufacture of golf balls, tobacco pouches, etc. It is said to be vulcanizable at 260 degrees F. An English patent was applied for by F. E. MacMahon.

**METALINED RUBBER.**—A name used for compounds used in dental work, under a process patented by C. S. Leadbetter, Manchester, England, for strengthening the gum with a metallic fabric, woven or knit.

#### MINERAL RUBBERS.

SO-CALLED mineral rubbers are chemically classed as hydrocarbons. This term is a convenient designation for any compound containing only hydrogen and carbon. Certain groups of such bodies, both native and artificial, have been for years in common use as ingredients in rubber mixtures.

The adaptability of these bituminous substances to rubber compounding is due to their possessing to a greater or lesser degree certain physical resemblances to india rubber, especially plasticity and a low melting point. These characteristics permit the bitumens to be combined easily with rubber and earthy matters and in this way very considerably assist the mixing of otherwise overcompounded or utterly unmixable stocks. Such hydrocarbons being practically proof against oxidation and inert to chemical action, are entirely harmless as affecting the durability of the stock. They may be credited with actually having a beneficial effect, inasmuch as they not only add plasticity to the stock and retard its rapid drying before vulcanization, but they fill the space otherwise occupied by, and exclude much of, the air which is always included to a considerable extent in every rubber mixing. By thus excluding air, the hydrocarbons practically lessen internal oxidation and in consequence the durability of the goods is increased. It has been demonstrated experimentally that certain of the solid "mineral rubbers" actually increase the tensile strength in mixings under favorable conditions.

There is a recognized place and value for both liquid and solid hydrocarbons in the manufacture of rubber stocks, but they ought always to be considered as "assistants" rather than as substitutes for rubber, which they are not.

Among the bituminous substances usually referred to as mineral rubbers are the following hydrocarbons, the specific gravities of which are about 1.05:

**ELATERITE.**—A natural mineral bituminous hydrocarbon.

**ELATERON.**—A hydrocarbon combination, in granular form,



blending with crude rubber without depreciating the peculiar properties of the latter.

EMAREX.—A product of a semi-elastic material similar to elaterite which by chemical treatment is made stable and tractable. It is wholly neutral, is free from sulphur and acids, and does not vaporize under heat. Is largely used in rubber compounding. Marketed in granular form.

GENASCO HYDROCARBON.—A product made from natural high-grade asphalt so treated that it is valuable in rubber compounding.

GILSONITE.—Lustrous black, hard bitumen. Found in Utah.

GRAHAMITE.—Dull black solid bitumen. Found in West Va.

KAPAK OR RAVEN MINERAL RUBBER.—A product made from treated elaterite. Used in general rubber compounding.

LA BELLE'S MINERAL RUBBER.—A treated elaterite produced by an inventor in Utah.

LIQUID RUBBER.—A compounding material for mechanical rubber goods, friction and cement stocks. It is said to be a synthetic composition of that class of terpene substances which belong to the caoutchouc family and react with sulphur in the same way that rubber does. In appearance, it is a lustrous, viscous liquid and extremely sticky.

PIONEER MINERAL RUBBER.—One of the first successful asphaltum rubbers used in connection with rubber compounding. It unites perfectly with any grade of crude rubber or with reclaimed rubber. Is said to prevent blistering, and to minimize the harsh action of free sulphur; is acid proof.

#### RUBBER SUBSTITUTES.

MOROCCOLINE.—An imitation leather made from a secret compound which presumably has india rubber for its base. Made in various colors, but chiefly as an imitation of Morocco leather.

NIGRUM ELASTICUM.—A sulphurized oil substance apparently made from linseed oil. Very dark colored and quite hard. Of English origin.

NOVELTY RUBBER.—An English substitute invented by David Lang. It is made in red and drab colors. It comes in small slabs about 18 inches square and 2 inches thick, weighing about

7 pounds. It is said to be easily mixed with ordinary rubber, vulcanized in the usual way, the price being about the same as for reclaimed rubber.

OHMLAC.—A hydrocarbon put up in different consistencies to suit varying compounding needs.

OKONITE.—A well-known compound for insulating wires and cables. According to an English analyst, it consists of india rubber 49.6 per cent.; sulphur 5.3 per cent.; lampblack 3.2 per cent.; zinc oxide 15.5 per cent.; litharge 26.3 per cent.; and silica 0.1 per cent.

OXOLIN.—An English invention patented by Charles J. Grist, an electrical engineer, and identical with "perchoid" in the United States. This gum is used for waterproof sheeting, printers' blankets, packings, etc. It is made of a solution of partially oxidized oil by adding litharge and heating to over 400 degrees F. Jute, or other fibers, is then dipped in the oil, the surplus oil is removed in a hydro-extractor, and the oil remaining on the fibers is oxidized by a current of air. These operations are repeated twice. The material is then ground with sulphur and coloring matters, and treated like india rubber.

PARAGOL.—A high-grade corn oil substitute.

PARKESINE.—Made from a compound of linseed oil and pyroxyline, and used in the manufacture of small articles that are sometimes made of hard rubber. A parkesine compound for molding, proofing, etc., is as follows: To 500 pounds water add 50 pounds sulphuric acid, and steep it in as much cotton, or rags, or jute, or linen as the liquor will moisten, for 3 or 4 hours. Take out, drain, and expose the mass to steam heat of about 280 degrees F., for an hour, if cotton or jute fiber has been used, and 3 hours if flax. Neutralize the acid pulp with a bath of water and soda, using 4 pounds of carbonate of soda to every 200 pounds of rags. Wash and press, pass through a coarse sieve of 12 meshes per inch, and dry. Grind the granulated material and sift it through a sieve of 120 meshes to the inch. The resulting powder may be mixed, in all proportions up to equal parts, with fresh rubber. Compounding 25 to 50 parts dry parkesine, with 50 parts alcoholic solvent. A proofing compound is: 1 pound paraffin, linseed oil, or other drying oil; 4 to 8 ounces parkesine.

**PEDRYOID.**—A rubber-like finish for cloth, made presumably of oil, in tan, brown, olive, and other colors, and used chiefly in shoe finishing.

**PENSA'S RUBBER.**—A French substitute made as follows: 100 parts of boiling coal tar, petroleum tar, oil of turpentine, or mineral oils, and 25 parts of boric, or phosphoric acid dissolved in alcohol, and the vapors are ignited, and the flame extinguished as soon as a green color is seen. The mixture is then heated at 60 degrees C. in the presence of oxygen, until a viscous ductile substance is obtained.

**PERCHOID.**—See Oxolin.

**PEROXIDE SUBSTITUTES.**—Peroxide of lead having been recommended as a better drier than other oxides used in connection with all compounds, the following formulas are given: 25 parts of walnut oil, 62 parts linseed oil, 5.5 parts peroxide of lead, 7.5 parts sulphur. One of greater toughness is composed of 25 parts walnut oil, 56 parts linseed oil, 5 parts peroxide of lead, 6 parts sulphur, 6 parts gum juniper.

**PICKEUM SUBSTITUTE.**—This is made by the following treatment of Pickeum gum:

A	
Boiled linseed oil .....	160 pounds.
Vaseline .....	20 pounds.
Bastard gum (or Pickeum gum) from Central America, cut fine .....	40 pounds.

Stir and heat to 250 degrees to 300 degrees F., until the gum is dissolved. Then cool to 100 degrees F., and strain.

B		
Mixture of {	Solution as above .....	5 gallons.
	Protochloride of sulphur .....	9 pounds.
	Bisulphide of carbon .....	9 pounds.

After the chemical action takes place, the mass is granulated and the grains are washed and stored for use, or the material may be masticated in a rubber mill and run into sheets for use.

**PURCELLITE.**—The invention of Dr. C. Purcell Taylor, of England. An insulating substance somewhat similar to gutta-percha, but costing much less. It is said to be very tough and elastic, may be made of any color, and is either flexible or rigid.

The specific gravity of the material is 1.2. It can be molded or vulcanized like india rubber. Its insulation resistance is equal to that of gutta-percha. It is unaffected by atmosphere, by alkaline or acid liquids, freezing mixtures and the like.

**QUINN'S RUBBER.**—An English substitute made from petroleum, bisulphide of carbon, chloride of sulphur, and rapeseed oil.

**RATHITE.**—A mixture in which waste silk fibers are incorporated with india rubber to impart resiliency and durability. About 6 ounces of silk are used with 28 pounds of rubber compound. It is employed in making tires, pump valves, packings, etc. Patented by A. I. Rath, Cheshire, England.

**RESINOLINES.**—Substances so called by Eugene Cadoret, of Paris, who obtains them by saponifying various oils by the use of a metallic carbonate, using by preference carbonate of lead, then decomposing by nitric acid, decanting, and saturating with an alkali. The soap thus formed is treated with acid to form a resinoid body, purified by dissolving in alcohol, and evaporating the solution. Resinolines thus formed are very similar to natural resins. They are either semi-fluid, pasty, or solid. When solid, they are remarkable for their flexibility.

**RHEA GUM.**—Rhea fiber washed and dried; immersed in a solution of silicate of soda; then carefully dried; then immersed in a bath of resin or other heavy hydrocarbon oil at a temperature of about 275 degrees F.; then put in a hydro-extractor which is worked at a temperature of 300 degrees F., when the superfluous oil is extracted; the mass is then dried. Later it is mixed with gums, resins, india rubber, or gutta-percha, and rhea gum is the result.

**RICE RUBBER.**—Japanese or Machi rice treated so that it makes an elastic cellulose product.

**ROSALINE.**—A vegetable product said to contain about the same chemical elements as india rubber, and of about the same specific gravity. Manufactured in the United States, France, and England. A strong point is made by the manufacturers that after vulcanization no chemist is able to detect that there is anything but pure rubber in a mixture containing 25 per cent. of rosaline and 75 per cent. of india rubber. In vulcanizing, it

requires about one-third more time to bring about the usual result.

**RUBBERAID.**—An amber-colored substitute manufactured from cottonseed oil by a secret process, which removes what the inventor calls the grease, leaving an elastic semi-solid which has been used quite largely in compounding.

**RUBBER ASPHALT.**—For road making, a late French patent covers a mixture of rubber and asphalt, that after intimate mixture takes the form of a powder. This is laid hot and under test is very cheap and lasting.

**RUBBER FLUX.**—A semi-fluid compound of a dark color and presumably made from non-drying, non-volatile oils. It is used in compounding where the stocks are dry, in place of palm oil, for example. Is said to prevent oxidation and bloom.

**RUBBERIC.**—Fiber blended with india rubber in solution, stretched, and dried. Used chiefly in making rubber tires and mechanical goods. Patented by William Golding, Manchester, England.

**RUBBERITE.**—An artificial rubber of the same specific gravity as fine Para. In color, elasticity, capability for vulcanization, and durability, it is said to resemble the higher grades of rubber. It is the invention of H. C. B. Graves, London, England, and is made up as follows:

Trinidad asphalt .....	47 to 80 per cent.
Oxidized oil .....	20 to 30 per cent.
Vaseline .....	5 per cent.
Sulphur .....	15 per cent.
Chloride of sulphur .....	3 per cent.

**RUBBER VELVET.**—Manufactured by sprinkling powdered felt of a variety of colors over proofed cloth before vulcanization. The result is a velvet-like fabric, elastic and waterproof.

**RUBERINE.**—An American rubber-like solution used as an insulation paint, and also as a proofing mixture, and partaking of many of the qualities of ruberoid. It is also manufactured in Germany.

**RUBEROID.**—An American substitute for india rubber that has the physical appearance of a high grade of black oil substitute. In use, however, it differs from many of them, for the



reason that it has been found useful in vulcanite compounds, while at the same time it may be used in ordinary soft rubber work.

RUB-HIDE.—This is a patented composition made from raw hide. It is very rubbery in consistency.

RUSSIAN SUBSTITUTE.—Manufactured from the skins of rabbits and other small animals, or the waste therefrom, digested in crude glycerine, and a little water. The formula is 3 parts by weight of the cleansed substance melted in water, with 3 parts by weight of crude glycerine, to which is added  $\frac{1}{4}$  part by weight of a concentrated solution of potassium chromate. The resultant mass is flexible. To make it harder, a little less glycerine and more chromate of potash are required. To withstand acids, 30 per cent. of gum lac dissolved in alcohol is added. For waterproofing fabrics,  $\frac{1}{4}$  part by weight of oxgall is added, with enough salt water to give it the consistency of oil.

SARCO.—A rubber assistant, probably made from treated elaterite.

SOAP SUBSTITUTES.—These have been exploited and explained more thoroughly by Professor W. Lascelles-Scott than by anybody else. The typical formulas that he gives are as follows: 28 parts of aluminum soap, 60 parts of linseed oil, 8 parts of acid free sulphur, 4 parts of oil of turpentine. Another, to use in connection with reclaimed rubber, is 15 parts of aluminum soap, 25 parts of devulcanized rubber, 60 parts fresh rubber, benzine *quantum sufficit*. Another still, in which a low grade pseudo-gutta is used, is 15 parts aluminum soap, 25 parts Almeida gum, 5 parts raw rubber, 6 parts sulphur, and 4 parts oleum succini.

SOLICUM.—A substitute or rather a compound patented by a chemist in Copenhagen. The basis of the discovery is waste rubber and oil.

SULO.—A sulphur oil substitute manufactured in the United States.

TABBYITE.—A mineral product from Utah which seems to be a mixture of asphalt and paraffin oils. It is easily manipulated and quite elastic.

TEXTILOID.—A mixture of a resinoline (as described by Cadoret under that heading) with natural resins, cellulose, nitro-cellulose, or organic substances of animal origin. The resultant material may be transparent, white, or colored. It is practically unflammable, has no smell, is very elastic, and, if submitted to heat, softens, and can be easily drawn out into fine threads. It can be used for waterproofing and in various other ways is a good substitute for india rubber. It is flexible and elastic. Textiloid is made of 4 parts resinoline, 2 parts nitro-cellulose, and 1 part camphor dissolved in alcohol at 90 degrees F. The result thus formed may be made in colors by the addition of metallic oxides.

THESKELON CEMENT.—A metallic substance used for waterproofing and for certain kinds of packings. It will neither expand, contract, nor rust. It is used instead of wax for sealing purposes, and resists acids, alkalies, and grease. It is often used in place of asphaltum. It can be mixed with tar, pitch, asphaltum, and other similar ingredients, the compound possessing extraordinary adhesive power. Patented by Thomas Smith, London.

TONG OIL SUBSTITUTES.—Manufactured from the Chinese oil known as tong oil, or wood oil. The oil is heated without any foreign matter being added to it, at a temperature of 250 degrees C., when it becomes solidified. It is then pulverized, and impregnated with petroleum, which swells it, and renders it more easily worked. Patented by Dr. Charpes Repin, Paris.

TREMENOL.—A German invention that has reference to the production of sulphonic acids, sulphones, oils, resin oils, mineral waxes, etc. Results from a treatment of mineral matter with fuming sulphuric acids at ordinary temperatures, or with concentrated sulphuric acid at 120 degrees C. The invention further calls for the treating similarly of the bodies obtained from the oil in their precipitation by means of sulphuric acid. The products are then washed in brine and water. The inventors precipitate glue and gelatine from a slightly acid solution as elastic rubber-like substances that can be drawn into threads with perfect ease.

TURNBULL'S ANTI-FOULING RUBBER PAINT.—Pitch and resin are melted together and then a mixture consisting of crude

naphtha, dissolved Para rubber, and sifted whiting is added thereto.

**TURPENTINE RUBBER.**—Manufactured by passing spirits of turpentine through a heated tube so as to vaporize it, and mixing the vapor with hydrochloric or other acid, so as to condense and solidify all of the vapor. Patented by A. F. St. George, England.

**UNVULCANIZED PACKING WASHERS.**—Goldstein claims in an English patent a washer material for the sheet-metal lids of vessels is made, without containing sulphur, of a mixture of crude rubber, talc, asbestos, and gutta-percha.

**VELVRIL.**—Basis, a drying or semi-drying oil; treated with strong nitric acid. This is compounded with nitrocellulose. By varying the proportions any consistency may be obtained from that of vulcanite to a soft, elastic, rubber-like substance. The product is nearly colorless in thin layers, which shows an elasticity of about 25 per cent., but no greater resilience. Invented by W. F. Reid, of England.

**VOLENITE.**—A substitute for india rubber and gutta-percha invented by Frederick Lamplough, United States. The compound is said to be a mixture of resins, or resin oil conveyed into a mass of fibrous material by a suitable non-oxidizable oil. This latter oil is used simply as a vehicle to carry the resin to its place, the process being completed by the distillation of the non-oxidizable oil, and the oxidizing of the rest of the mass. The oil used is preferably a fish oil, which is refined carefully before use. After saturation and treatment the vegetable fiber is changed into a homogeneous mass which has many of the characteristics of vulcanite. A formula that is said to have worked well is 10 parts by weight of fiber, 5 parts resin oil, and 2 parts fish oil, treated at a temperature of 130 degrees C., for say  $4\frac{1}{2}$  hours.

**VOLTAX.**—An American insulating compound not subject to chemical change, and proof against water, acids, and alkalis. Is cheaper than rubber and does not affect copper—hence tinning of the wires is not necessary.

**VOLTIT.**—The base of this is glue or gelatine prepared from scraps of kid skins, which are treated until they reach a gela-

tinous mass, which is filtered and mixed with oleic acid, the proportion being 80 parts of oleic acid to 20 parts of the gelatine. The mixture is boiled for  $\frac{1}{2}$  hour, and then 11 parts of caustic potash solution (in 50 parts of water) are added. The boiling is then continued for an hour, and a special mass is formed to which are added resin oil, oxidized linseed oil, and paraffin. The whole mixture is then boiled 4 to 5 hours. Also spelled voltite. It is of French origin.

VORITE.—A solid blown oil substitute containing no sulphur and no acid or free oil. The melting point for the soft grade is from 300 degrees to 400 degrees F., and for the harder grade 550 degrees F. It is a floating substitute and burns without leaving any ash. It is made in three grades, which are distinguished by the names soft, ground, and white. According to the makers it absolutely resists oxidation and drying out, and is already largely used in the manufacture of insulated wire and in general mechanical rubber goods.

VULCANINA.—A preparation of rubber, a Brazilian invention, for paving.

VULCANINE.—A mixture of india rubber, asbestos, litharge, lime, and powdered zinc, to which is added a percentage of sulphur. Mentioned in a patent granted to J. E. Hopkinson, West Drayton, England.

WATERPROOF GLUE.—A substitute for canvas proofing made as follows: Dissolve 16 ounces of glue in 3 pints of skim milk, and to increase its strength add a little powdered lime.

WHALEITE.—See Woodite.

WHEAT RUBBER.—See Cereal Rubber.

WICHMANN'S SUBSTITUTE.—A combination of vegetable albumen and animal casein.

WINTHROP GUM.—Another name for rubberaid.

WOLFERT.—A substitute for rubber made of felt impregnated with a waterproof substance, presumably vulcanized oil. An English invention.

WOODITE.—A name suggested by Sir E. J. Reed for an india rubber compound invented by Mrs. A. M. Wood. It is said to possess the elasticity of india rubber, to be uninflam-

mable, and not injured by salt water. It is used in making valves, packings, etc. It is claimed that it will not become sticky or soft under heat or steam pressure, and will stand hot grease and other lubricants, and neither acids, alkalies, nor wastes from oil refineries, distilleries, etc., affect it in the least. A compound for woodite or whaleite packing is: asbestos fiber 38 pounds, asbestos powder 38 pounds, earth wax 6 pounds, charcoal finely ground 9 pounds, ground whalebone 20 pounds, Para rubber 80 pounds, and sulphur 5 pounds.

ZACKINGUMMI.—Substitute invented by Zachias Olsson, a Swedish chemist. Consists of a mixture of glycerine, chloride of calcium, magnesium, and paraffin.

ZINSSER'S BARREL LINING.—A compound for lining casks, consisting of deodorized copal, rosin, india rubber, and a non-drying fat, with coloring matter, such as asphalt.



## CHAPTER VIII.

### SUBSTITUTES FOR HARD RUBBER AND GUTTA-PERCHA, INCLUDING CELLULOSE PRODUCTS.

HARD RUBBER in its best estate is so valuable and perfect a product that it would always have the preference were it not for its unavoidable high cost. Because of this cost there are many substitutes for it that counterfeit it in texture, color, and quality, but are never quite its equal in all these points of excellence. These substitutes are made of cellulose, gums, and animal, vegetable, and earthy matters, having a variety of distinctive names and varied uses. To the popular mind, if they look like ebonite, they are hard rubber. In the same way, gutta-percha is often confounded with hard rubber; which it resembles under many conditions. The following list covers not only certain widely known compounds of hard rubber and gutta-percha, but a number of substitutes for them are now put to many uses, the chief of which, perhaps, is insulation.

ALEXITE.—An American insulating material which can be molded in any shape, is waterproof, fireproof, and acid proof, and can be produced in any color. In texture and general appearance it resembles vulcanite.

AMBROIN.—A German substitute for hard rubber, consisting of fiber, silica, and resin compressed to a mass. Its color varies from light brown to green or black. Nitric and acetic acids do not affect it, and even aqua regia does not injure it. Under a moderate heat it softens slightly and can be worked, like vulcanite, in a mold. It also takes a bright finish from the buffing wheel.

ARMALAC.—See Insulac.

ARTIFICIAL WHALEBONE.—A well-known product made as follows: india rubber 20 parts, sulphur 5 parts, shellac 4 parts, magnesia 4 parts, and gold brimstone 5 parts. Vulcanized somewhat the same as hard rubber.

**BAKELITE.**—A patented substance said to have the combined properties of amber, celluloid, and hard rubber. The invention of Dr. L. E. Baekeland. It is a compound or condensation product of formaldehyde and phenol or carbolic acid. It has long been known to chemists that formaldehyde and phenol formed condensation products which have been put on the market as artificial gums and resins and used to some extent. It was further known that by a certain process this material was condensed into a hard, resinous body which resisted every known chemical solvent and was only changed by actual burning. This substance was usually porous and was of no value. Dr. Baekeland discovered that, by carrying on the process in a vulcanizer where heat and temperature conditions could be controlled, the reaction could be divided into several stages, producing first a plastic mass which can be molded or carved, and on further treatment in the vulcanizer where it is submitted with certain chemicals to carefully regulated conditions of heat and pressure, that a hard, transparent substance could be produced which is most inert chemically. Bakelite resembles physically and possibly chemically the Chinese or Japanese lacquer. It is manufactured into a large variety of electrical goods such as terminals, high potential insulators and, in its liquid form, is used to impregnate armature and other coils, the impregnated material being subsequently converted by heat into the hard form.

Bakelite takes a high polish and machines freely. It is well adapted to manufacture in rubber works, as most of the machinery can be used with little change.

**BALENITE**, as the name signifies, is intended as a substitute for whalebone. It is quite elastic; in other words, it is neither hard nor soft, but may be characterized as semi-hard. A well-known compound for this is india rubber 100 parts, shellac 20 parts, burned magnesia 20 parts, sulphur 25 parts, and orpiment 20 parts. (Hoffer.)

**BETITE.**—An English insulating material which is said to be bitumen refined to absolute purity and vulcanized. It is used on cables, in underground work, for low pressure resistance, and in rare instances for high pressure.

**BROOKSITE.**—A compound of resin and heavy resin oils for insulating purposes.

**BROWN'S SUBSTITUTE FOR HARD RUBBER.**—Made of bitumen sulphur, lead peroxide, and gum camphor. Amalgamated by heat.

**CAOUTCHOUC ALUTA.**—A composition used as a substitute for hard rubber, made of leather scraps boiled in water, with a sufficient quantity of oxalic acid to dissolve them, and a portion of glue. To this are added resin, pitch, beeswax, and copal gum, dissolved in oil. India rubber boiled in linseed oil is then added and a powder formed of plaster of Paris, and a coloring matter is stirred into the composition to thicken and stiffen it.

**CARBO-NITE.**—A cottonseed oil preparation intended as a substitute for hard rubber.

**CELLIT.**—A cellulose acetate. The invention of a German chemist, designed to take the place of celluloid, but to be more easily worked and safer by varying the organic substance that takes the place of camphor. A great variety of products is produced. The substance varies from a soft plastic to a hard product according to the degree of compound used.

**CELLULITH.**—A cellulose substitute said to be an improvement on viscid. Mixes readily with shellac, rubber, etc.

**CELLULOID** is made in the main from camphor and nitro-cellulose in alcohol, ether being sometimes employed as an additional solvent. The paste formed in this way is warmed gently, and then rolled out into thin sheets. The product is a brittle, horny mass, consisting of a chemical, or at least an intimate, mixture of camphor and pyroxylin. Ordinarily it is highly inflammable. A great variety of coloring matters may be added to it and it is susceptible to manipulation and processes whereby it has been made quite flexible and practically incombustible. Crude celluloid has a specific gravity varying between 1.25 and 1.45, and has a strong odor of camphor.

**CELLULOSE** is a pure substance forming the cellular tissue of plants. Specific gravity 1.53. In the arts use is made generally of cotton or filter paper which has been treated with acids to dissolve out impurities, and forms a basis for the manufacture

of celluloid, gun cotton, pyroxylin, and xylonite. On analysis it shows: carbon 44.44, hydrogen 6.18, oxygen 49.38. It is dissolved in sulphuric acid, and is converted into dextrine, and, by prolonging the action, into glucose. So far it has not been used largely in rubber compounding, but both alone and in connection with various other ingredients has been applied as a waterproofing. It is the basis of certain Swiss puncture fluids.

CE-RE-GUM.—A compound made by a secret process, and which, vulcanized, produces a fairly good imitation of hard rubber. Invention of H. W. Morgan, United States.

CHATTERTON'S COMPOUND.—A widely known compound sold the world over for connections for joint sheets and for uniting gutta-percha parts, and also for cementing gutta-percha to wood. It softens readily at 100 degrees F., and becomes firm again when cold. Its specific gravity is about 1.02. The best compound is 1 part by weight of Stockholm tar, 1 part resin, and 3 parts cleansed gutta-percha, melted and mixed.

CONDENSITE is a phenolic condensation product invented by J. W. Aylsworth, who for more than a quarter of a century was associated with Thomas A. Edison, as his chief consulting chemist.

Condensite was developed in the course of a search for a better material to be used in the manufacture of phonograph records. It is the only phenolic condensation product that has ever been successfully used in the making of a record, which is probably the most difficult plastic molded article to manufacture without imperfections.

Condensite is unlike any other phenolic condensation product, because of the unique method by which it is made. By this process the product, during the reaction between the chemicals of which it is composed, is heated to such a degree as to dissociate all the water.

The absence of water, even in minute quantities, gives to the final product, a capacity for taking extremely minute impressions in molding, as well as imparting to them unusual electrical and other qualities of value.

The next step in the manufacture of condensite very much resembles that of rubber manufacture. It is compounded with

a chemical that reacts upon it when heated, and hardens the product, just as sulphur or other vulcanizing mediums harden rubber when similarly treated, and the process of molding is very much the same as in rubber manufacture.

Condensite has in some instances been used in the place of rubber, but its development has chiefly been in competition with other substances, and with respect to rubber rather supplements than serves as a substitute for it. Each possesses valuable properties not found in the other.

CORALITE.—A name for vulcanite which is colored to imitate coral.

CORIMITE is a solid substance derived from fish offal through a process recently invented by a Danish chemist, and said to be particularly suitable for electric insulation.

CORNITE.—A specially hard vulcanite or hard rubber, so named from the Latin *cornu* (a horn).

DE PONT SUBSTITUTES.—An English patented product made from asbestos 30 parts, plaster of Paris 5 parts, clay 8 parts, copal 15 parts, tar 5 parts, bitumen 15 parts, aniline 2 parts, lampblack 15 parts, mica 4 parts, wax 3 parts.

DIATITE.—A combination of diatomaceous earth, and shellac, made under very heavy pressure. It may be made of any color, and is used as a substitute for hard rubber.

EBONITINE.—A hard rubber substitute formerly used for phonograph records. Is of a brilliant black color. Said to be a good insulator and resists acids. Of German origin.

ELECTROSE.—A substitute for hard rubber for which the following advantages are claimed: It will not tarnish metal, as no sulphur is used in its vulcanization; it is cheaper than hard rubber; it possesses high insulation properties; it can be melted readily into any shape, or made of any color; it does not fade; it possesses great strength, and takes a high polish; changes of temperature do not affect it; and it withstands the weaker acids and alkalies.

ESBENITE.—Made of pure cellulose, chemically incorporated with mica in the form of fine powder, with the addition of magnesia and a silicate, thus forming strong and close grained artificial mica. It is flexible, and can be molded into any shape.



Esbenite is waterproof, does not burn readily, and is thoroughly airproof. Manufactured in England.

**FIBRONE.**—A substitute for hard rubber which is a good non-conductor, waterproof, and can be handled in a lathe like vulcanite. It is said to be durable, does not contract or expand, and is made in all colors. It is used for thumbscrews, pushbuttons, etc. Plasticon is similar to fibrone, but heavier and of a more stony nature, and probably made of the same material.

**GALALITH.**—A German product from casein. The process roughly is to make the casein insoluble by the addition of salts and acids. The product is then dehydrated and dried, when, by the addition of formaldehyde, galalith is obtained. The process is protected by numerous patents.

**GUN COTTON.**—Prepared by treating cotton wool with a mixture of strong sulphuric and nitric acids, or nitrate of potash may be substituted for nitric acid. After treatment with acid the gun cotton is rinsed carefully in cold running water, and then dried by pressure or by exposure to the air. All acid should be removed to prevent danger of explosion. Gun cotton has been used to render fabrics waterproof, for varnishing india rubber to render it impervious to gases, and in insulation work. Alexander Parkes, as far back as 1855, used a solution of gun cotton with gums or resins to take the place of compounds of india rubber. He rendered gun cotton less inflammable by using biphosphate of ammonia, magnesia, talc, alum, or similar substances. As a good solvent for gun cotton, he distilled in 1 gallon of naphtha from 2 to 6 pounds of chloride of calcium. Charles Macintosh used as a solvent equal parts of wood spirit and coal tar naphtha.

**HARD CORE FOR GOLF BALLS.**—An English composition which consists of 100 parts calcium chloride, 25 parts chloride of zinc, 100 parts potato starch.

**HYALINE.**—Made of a mixture of equal parts of gun cotton and a variety of resins. The gun cotton is dissolved in ether and the resins in solution are added, the result being a thick, gelatinous mass. When allowed to dry, this mass soon

hardens and forms a horny, incombustible material. Invented by Frederick Eckstein, Vienna.

INSOLACIT.—An insulating material produced either as a liquid, semi-liquid, or solid. It is not inflammable or affected by corrosive acids, alkalis, saline substances, etc. It is a German product and the compound remains a secret.

INSULATE.—A molding hard composition for electrical insulations, resembling other condensation products.

INSULLAC.—A spirit copal resin varnish, with the acids of the resins neutralized as much as possible, to prevent the resin acids from attacking the copper wire. It is a transparent elastic material, and is superior to shellac. Armalac is made of black paraffin wax, in solution in petroleum. It remains permanently plastic under heat, although it dries quickly and thoroughly. Manufactured in the United States.

ISOLATINE.—An American insulating material prepared especially for high resistance. It is said to be flexible, not to be affected by cold or heat unless the latter is artificial, and to be durable. It is also said to protect metal.

KASENOID.—An English substitute for ebonite, galalith and zylonite for many purposes. The properties are quite similar to those of galalith—it is tough, resilient, non-inflammable, a good insulator, capable of being molded, and is made in a variety of colors, either as sheet or rod. It can be turned and polished and takes an excellent thread.

KEMPEFF HARD RUBBER SUBSTITUTE.—A mixture consisting of 20 per cent. resin and asphaltum, 15 per cent. china clay, 11 per cent. kieselguhr. Mixture is allowed to cool; ground dry; with 4 per cent. of sulphur, and 50 per cent. of ground asbestos fiber. It is elastic and unaffected by acids.

KERATITE.—Another name for hard rubber, derived from the Greek word meaning horn.

KERATOL.—An American waterproof preparation, not of the nature of rubber, but probably one of the cellulose substitutes. It is a colorless transparent substance, and when applied to fabrics renders them waterproof and prevents crocking and fading. It also strengthens the fabric, and allows stains

to be washed off. An artificial leather is also made of Keratol. The name is adapted from the Greek word *keros*, meaning hornlike.

**KIEL COMPOUNDS.**—One of these well-known compositions consists of india rubber, sulphur, pumice stone, oil, and beeswax. The product is a hard rubber, said to possess a superior elasticity and toughness, and capable of being vulcanized in sheets at least  $2\frac{1}{2}$  inches thick. This compound is not affected by the most intense cold, and will stand a higher temperature than ordinary rubber. It also burns with difficulty. Its ingredients are said to mix faster and more uniformly than those of other compounds. It resists acids, and other corrosive substances, is a perfect insulating material, and is cheap. Another Kiel compound is made of india rubber, sulphur, and mineral oil. It is more flexible than ordinary hard rubber, and when warm is more plastic than such compounds. It is also less brittle and cheaper, and can be turned in a lathe with greater facility and less injury to the tools.

**KORNITE.**—A Russian substitute for hard rubber made at Riga. It consists of 25 per cent. of prepared fish bone and 75 per cent. of scrap horn ground to dust, and then melted under high pressure and steam heat.

**LACTITIS.**—An artificial ivory made from milk, the process being coagulation, straining, and rejection of the whey. Ten pounds of the curd are then taken and mixed with the solution of 3 pounds of borax in 3 quarts of water. The mixture is then placed in a vessel over slow fire and left until it separates into two parts, one as thin as water, the other resembling melted gelatine. The watery part is drawn off, and to the residue is added a solution of 1 pound of mineral salt in 3 pints of water. (Sugar of lead answers very well as the mineral salt.) This brings about another separation of the mass, into a liquid and a mushy solid. The liquid is strained or filtered off, and at this point coloring matter may be added. The solid is now subjected to heavy pressure in molds of any shape, and afterwards dried under great heat. The resulting product may be used in the manufacture of billiard balls, knife handles, or anything for which ebonite or celluloid is adapted.

**LAMINA FIBER.**—An American invention, used chiefly for electrical purposes. It is of various colors, heavier than vulcanized rubber, and swells to nearly double its weight when placed in water. It is probably a cellulose compound containing no rubber.

**LEATHEROID.**—A mixture of American origin, made in black, red and gray, and similar to vulcanized fiber. It is insoluble in ordinary solvents, uninjured by alcohol, ether, ammonia, turpentine, naphtha, or other oils; is very tough, a good insulator, and of low cost.

**MARLOID.**—An insulating material said to be made from the hides of certain animals, treated by a chemical process, making it so hard that it can be handled in every way the same as ebonite. It may be transparent or opaque, and is capable of receiving a very high polish. It is said to give an insulation of 2,000 megohms, is unflammable, and of English origin.

**MICANITE.**—Mica cemented together under pressure with an india rubber compound. Manufactured in America.

**NIGRITE.**—An insulating compound consisting of a mixture of india rubber and ozocerite.

**NITROCELLULOSE.**—This is produced by the action upon cellulose of nitric acid or a mixture of nitric and sulphuric acids. According to the length of time the acid is allowed to act, the resulting nitrocellulose contains 53.7, 43.6, 36.7 or 28 per cent. of nitric acid (nitric-anhydride). Gun cotton is usually a mixture containing higher percentages, while pyroxylin—or, as it is sometimes called, soluble cotton—is a mixture of lower compounds. The solution of pyroxylin in a mixture of alcohol and ether is called collodion.

**PANTASOTE.**—A cellulose product largely used in the manufacture of artificial leathers.

**PEGAMOID.**—This, although covered by several patents, is said also to involve certain secret processes. In a general way, however, the substance is prepared by treating a fine grade of cellulose with a mixture of sulphuric or nitric acid to form nitrocellulose or gun cotton, which is then dissolved in a suitable alcohol. The pegamoid patents call for the addition of glycerine, sweet or olive oil, and various coloring matters.

PLASTICON.—See Fibrone.

PLASTITE.—A vulcanite which is made extra hard and is not possessed of any special amount of elasticity. The stock recipe for this is: india rubber 100 parts, sulphur 25 parts, magnesia 50 parts, orpiment 50 parts, coal tar asphaltum 60 parts. It is very hard and solid, and takes a high degree of smoothness and polish. (Hoffer.)

POTATO CELLULOID.—An Austrian invention relating to an artificial solid produced from potatoes boiled 36 hours in a fluid containing 8 parts of sulphuric acid and 100 parts of water, and then dried. Pipe bowls made from it for the French market are said to be hardly distinguishable from real meerschaum. Billiard balls are also said to be made from it.

PRESSPAHM.—An English insulating material made from wood fiber so treated that it can be run through rolls into sheets of varying thicknesses. It is said to be capable of withstanding high temperatures, and is used not only in connection with electrical machinery, but also for bookbinding and for putting a finish on cloth.

PYROXYLIN.—A species of gun cotton less explosive in its qualities, prepared from cellulose by means of nitro-sulphuric acid. Its solution in a mixture of ether and alcohol is called collodion.

SILUMINITE.—This new insulating material, of English origin, is a hard black substance, ringing like slate, but of far greater strength; it can be sawed, filed, drilled, tapped, turned, and polished with ease, and can be molded to any shape in the course of manufacture but not afterwards. It is not softened by heat (it is subject to a temperature of more than 600 degrees F. at the makers' works) and is not brittle. Immersion in oil or caustic alkali, or boiling water, leaves it unchanged, and it is non-hygroscopic. It possesses high dielectric strength, this being between 10,000 and 13,000 volts per millimeter. Its structure is homogeneous and dense, the weight of a square foot  $\frac{1}{4}$ -inch thick, being 2.4 pounds. Metal parts can be insulated by compressing siluminite on them in any desired shape, thus avoiding the cementing or screwing process now necessary in most cases. The substances with which it will most directly



compete are porcelain, glass, mica, fiber, ebonite, wood, slate, marble and molded compounds. It is supplied in the form of rods, sheets, tubes and various molded specialties.

**SOREL'S COMPOUND.**—A so-called substitute for gutta-percha consisting of 2 parts resin, 2 parts asphaltum, 8 parts resin oil, 6 parts slaked lime, 3 parts water, 10 parts potter's clay, and 12 parts gutta-percha. Five per cent. of stearic acid is sometimes added.

**STABILIT.**—A German invention, the compound for which is a secret, designed to be half way between hard rubber and vulcanized fiber. It is not affected by corroding substances, and does not absorb moisture. It withstands boiling water where hard rubber and vulcanized fiber do not, and is not attacked by muriatic acid or sulphuric acid.

**TEXODERM.**—An imitation leather with a hard, durable waterproof surface. Basis of which is cellulose.

**VEGETALINE.**—Cellulose treated with sulphuric acid, dried and ground, then treated with resinate of soda.

**VISCOID.**—A compound of viscose, formed by mixing with it hot bituminous matter such as tar, pitch dissolved in coal tar, or the like. The resultant mixture, when solidified, constitutes a material of a high insulating character, and is produced at a low cost. The bituminous and cellulose matter may be mixed in equal proportions, although there is a wide range of compounds that may be made through the use of various proportions of the substances.

**VISCOSE.**—An English cellulose product, used as a substitute for vulcanite. It may be of any color or any degree of hardness. It has been used in connection with rubber, experimentally, with excellent results. As a friction for belting it is said to be excellent, whether or not the belt has the regulation rubber cover.

**VITRITE.**—A jet black, perfectly hard material, having a smooth polished appearance similar to ebonite. It is not affected by dampness or acids. It is a good insulator, is of low cost, and easily worked.

**VULCABESTON.**—A composition of asbestos and india rubber, forming a product which is a non-conductor of electricity and stands the severest tests, resisting heat wonderfully. Invented by R. N. Pratt, United States.

**VULCANIZED FIBER.**—This material, which is very largely used, is made of cotton paper pulp, chemically dissolved, and solidified under enormous pressure. It is unattacked by ordinary solvents such as alcohol, turpentine, ammonia, etc. It appears on the market in two forms—hard and flexible. The hard fiber resembles horn and is exceedingly tough and strong, while the flexible fiber has the appearance of a very close-grained leather. It is an insulator in dry places, but, as it will absorb moisture, it is useless in places requiring waterproof qualities. It is made in three colors—black, red, and gray. Vulcanized fiber is unaffected by oils or fats, and will stand action of hot grease. Low grades have been found adulterated with chloride of zinc and calcium, to the extent of nearly 50 per cent. of its weight.

**WEBER'S CELLULOSE COMPOUND.**—Ten pounds of cellulose steeped in a 20 per cent. solution of caustic soda and allowed to stand for ten hours; then pressed until its weight is 35 pounds; then treated with 8 pounds cold carbon bisulphide for three hours; then emulsified with a mixture of 40 pounds Pontianak gum, 15 pounds mineral oil, and 10 pounds stearine pitch.

**WILLOUGHBY SMITH'S GUTTA-PERCHA.**—Gutta-percha refined by a special process invented by Willoughby Smith. Valued in England as giving an increased speed over electrical conductors insulated with it.

**WRAY'S COMPOUND.**—A composition of india rubber, silica, powdered alum, and gutta-percha. Used in climates too hot for gutta-percha by itself. It is easily attacked by seawater.

**XELTON.**—A substitute for hard rubber manufactured principally for use in making battery jars. It originated in Philadelphia.

**XYLONITE.**—See Celluloid.

## CHAPTER IX.

### RESINS, BALSAMS, GUMS, EARTH WAXES, AND GUM-LIKE SUBSTANCES USED IN RUBBER COMPOUNDING.

A GREAT variety of vegetable, mineral, and animal resins and waxes find uses in admixture with india rubber and gutta-percha. Their important uses are to render compounds adhesive, as in frictions, to assist in insulation, to add luster, and to modify the texture of the vulcanized compound. Many gums, like many earths, lend special virtues which they possess to rubber compounds. The more important of these materials, and those most generally used, are described in the following pages.

ACACIA.—See Arabic, gum.

ACROIDES GUM, also known as Botany Bay gum or mineral lac, is the name given to the resins of the various branches of the *Xanthorrhæa* plant species.

Red gum acroides comes from the *Xanthorrhæa Australis* and *Arborea*. It forms flat pieces from one-half to one and one-half inches thick, sometimes as big as the hand, shows distinct traces of its structure and embraces unresinified tissues. It is reddish-brown in color, leaves an orange-red mark, smells somewhat like benzoin, and has an unpleasant taste like cinnamon.

Yellow gum acroides comes from the *Xanthorrhæa Hastilis*, forms round or oval pieces of various sizes, resembles gamboge on a fresh fracture, becomes covered with reddish-brown coating on exposure to the air, smells like benzoin, has a somewhat sweet or spicy taste, and contains in addition regular admixtures.

Both gums are soluble in acids and ether. They contain paracoumaric acid, benzoic acid, para-oxy-benzin-aldehyde and abietic acid, the yellow gum having also traces of cinnamic acid and styracin. They are used in the manufacture of sealing wax and colored varnishes which do not fade on exposure to the

light and which are suitable for painting the glasses of photographic dark-room lamps. They are also employed in making the better classes of soap; in the preparation of picric acid and paracoumaric acid, as well as in the linenizing of the thinner qualities of paper. For insulating purposes acroides is melted and mixed with other ingredients and molded to form insulating pieces for electrical apparatus. The exact process is a manufacturing secret.

Acroides was used in England in the eighteenth century as a medicine for the stomach, but it was not employed for manufacturing purposes until 1840 in England and 1860 on the Continent.

ADAMANTA RESIN.—An imitation copal, manufactured from common resin by a special hardening process. It is not soluble in alcohol or benzine, but completely so in boiling turpentine. It is free from acids and alkalies, and has the same melting point as Zanzibar copal. It is used rarely in rubber shoe varnish, and often in cheap frictions in mechanical lines, being moistened with resin oil to increase its adhesiveness.

AMBER.—A fossil resin chiefly found in Prussia, on the shores of the Baltic sea; it occurs also in Sicily and sometimes in the United States. It is the hardest and heaviest of the resins. Its specific gravity is about 1.07. By distillation a yellow oil—oleum succini or oil of amber—is obtained, and a yellow resin remains in the still. Amber varies in color from light yellow to a deep brownish-red. It is insoluble in almost all of the ordinary solvents. When heated above its melting point, however, it becomes partly decomposed, and is then soluble in oil of turpentine and alcohol. It makes a very fine transparent varnish, which is used on negatives in photographing. It is used in cements for fastening linoleum and rubber tiling to decks, and is also mentioned in the formulas for certain patented gums.

AMMONIACUM GUM.—Exclusively obtained from Persia as tears, or aggregated masses, of a peculiar smell and a taste slightly sweetish, bitter, and somewhat acrid. Its specific gravity is 1.207. Used in solutions for pressed leather cuttings and fibrous wastes. Ten parts of this gum mixed with 20 or 25

parts of gutta-percha form a cement possessing both elasticity and solidity, and is thoroughly waterproof; used for filling cracks in horses' hoofs. Also used with gutta-percha, boiled linseed oil, and dry casein or caseum, for sticking together small particles of any dry matter in the production of artificial leather.

ANIME is a South American fossil resin similar to copal. It occurs in small, irregular pieces of a pale yellow color. Has a high melting point, and its specific gravity is 1.028 to 1.072. Mixed with rubber and earthy matters and dissolved in turpentine, it formed one of the early compounds for clothing.

ARABIC GUM is exuded from a species of *Acacia*. It is made up of clear or semi-transparent fragments, hard and brittle, breaking with shining fracture. It is inodorous and feebly sweetish to the taste. Its specific gravity is 1.31 to 1.52, for dried gum. It comes from Africa and is known also as acacia and gum Senegal. It dissolves in hot or cold water. It is used in connection with plaster of Paris in making a tougher surface mold for small and experimental rubber work. Enough gum is added to make the mixing solution about the thickness of a thin syrup. It is largely used in cements. It is also used in certain shower-proof compounds and in paste blackings made of caoutchouc oil, vinegar, molasses, and boneblack.

ARKOSITE.—An infusible pure asphaltite. It is a valuable pigment for structural paint and in rubber goods.

ASPHALT is undoubtedly an oxidized residue from evaporated petroleum. Its specific gravity varies from 1.00 to 1.68. This name is applied usually to the solid bitumen, the liquid being called mineral tar, and sometimes maltha. It is chiefly made up of hydrocarbons, but contains a certain amount of sulphur and nitrogenous bodies. It is known also as natural pitch, Jews' pitch, asphaltum, bitumen, etc. It is a black, hard substance which, when freshly broken, shows shining surfaces that are always correspondingly rounding and hollowing. It is insoluble in water and alcohol, but dissolves in benzine, acetone, and carbon disulphide. Is used in rubber compounding in place of coal tar, and in insulating compositions, and in certain substitutes like kerite. Commercially there are two grades, known



as "lake pitch" and "land pitch," of which the latter is the harder.

In solution it is used sometimes to protect rubber goods that are exposed to the destructive influence of brine. A little asphalt is also said to increase the elasticity of hard rubber. Asphalt mixed with resin and oil of tar forms a low-grade artificial gutta-percha. It is added to "Cooley's artificial leather" to harden it and enable it to resist heat. It is also the basis of one type of marine glue.

ASPHALT, ARTIFICIAL.—This is made by heating sulphur and resin together to about 250 degrees C., where the reaction takes place, attended by the evolution of sulphuretted hydrogen, and leaving an almost black, pitchy substance resembling asphalt. It is insoluble in alcohol, but dissolves readily in benzene.

BALSAM.—This term is given to oleo resins which are soft at ordinary temperatures, and are really a mixture of such a resin and the essential oil of the plant from which they exude, such as benzoin, tolu, etc.

BALSAM OF STORAX (or STYRAX).—Produced from the inner bark of a tree of the genus *Storax*, in Asia Minor. Commercially it is a soft, coarse, dark-colored powder; or, more commonly, a semi-fluid, adhesive substance, brown outside, greenish-gray inside. The sweet gum of the southern United States is allied to the Eastern drug, and was formerly much used in chewing gum. Used in general cements, being particularly good in leather cements; also for glass, stone, and earthenware cements.

BALSAM OF SULPHUR.—A solution of sulphur in boiling volatile or olive oil. Used in certain rubber compounds as a vulcanizing agent and a protection against blooming.

BEESWAX is obtained from the comb built by honey bees. The crude wax is yellow and soft, with a granular fracture. Its specific gravity varies between .965 and .969, its melting point being between 140 degrees and 144 degrees F. It is often adulterated by water, by white mineral powders, and by cheaper substances, such as vegetable wax, paraffin, etc. White wax is that which has been exposed to the sun or to the moderate action of

nitric or chromic acid, thereby being bleached. It is sometimes used with rubber in medicinal plasters. Ordinary beeswax is largely used in Kiel's hard-rubber compounds. Sheet beeswax is often used in the work of vulcanite pattern making. It is also used in processes for making fabrics water-repellent, the other ingredients being alumina, resin, soap, wax, and silicate of soda. With gutta-percha it is an ingredient in shoemakers' wax, and also in certain proofing compounds. Hancock used it in a gutta-percha compound for a soft effect. In a hard rubber compound made up of india rubber, sulphur, oil, and pumice stone, it is said to be acid proof.

**BENZOIN.**—Occurs in lumps of yellowish brown tears, stuck together and more or less mottled from the white inside the tears. Its specific gravity is from 1.063 to 1.092. Of an agreeable balsamic odor and very little taste, but irritating when chewed for some time. Used in linseed oil proofings, presumably to kill odor; also in certain gutta-percha and india-rubber compounds for disguising the odors. Four per cent. of the weight of the mass is said to be sufficient to make the odor an agreeable one. According to Forster, a little of it mixed with gutta-percha greatly improves the quality.

**BIRCH-BARK TAR.**—A peculiar tar obtained during the distillation of birch-bark for oil, being probably the same as Russian jackten extract. Used in the manufacture of certain rubber substitutes. Specific gravity 1.82.

**BITUMEN.**—The term applied to a body made up of several hydrocarbons. It resembles Trinidad asphalt and is of the same nature. Its specific gravity is from 1.073 to 1.160. Artificially it is prepared from shales, mineral asphalt, etc. It is used as a source of paraffin. The West Indian product is known as chapapote. A solution is made from it in which the tapes are soaked that are used for covering wire that has been insulated with india rubber. Bitumen has been utilized by what is known as the calendar process, which is a partial vulcanization, rendering it valuable as an insulator.

**BITUMEN, AUVERGNE.**—A species of natural asphalt found in the province of Auvergne, France. It is similar to Trinidad asphalt, but is impure, containing clay, silica, magnesia, iron, and traces of arsenic. See Asphalt.

**BLACK PITCH.**—Is the residue left after the oils of tar have been distilled from that body. Used in weather-proofing work.

**BRITISH GUM.**—See Dextrine.

**BURGUNDY PITCH.**—Is obtained from the hardened juice or sap which concretes upon the bark of the Norway spruce. Specific gravity 1.07-1.10. As imported it is often quite impure and should be melted and strained before being used. It is almost entirely soluble in glacial acetic acid or boiling alcohol, and somewhat in cold alcohol. When pure it is hard and brittle, with a shining fracture, dissolves in benzine, acetone, and carbon disulphide. Is usually reddish or yellowish-brown, aromatic. It is much used in cements, in electric tape, and in the manufacture of porous plasters. Common resin is often melted and mixed with fats and water, forming a gum that much resembles Burgundy pitch.

**BURMITE AMBER.**—Found in Burma, but quite inferior in quality. It is a little harder than amber proper, is easily cut, takes an excellent polish, but has less variety of color. See Amber.

**BUTTON LAC.**—See Shellac.

**CAMPHOR.**—The white transparent substance known by this name is obtained from Japan and the island of Formosa. It is really an oxygenated essential oil. Its specific gravity is 0.985. Sparingly soluble in water, and very soluble in alcohol, ether, acetic acid, and hydrocarbons or volatile oils. Is largely used in the manufacture of celluloid. Gum camphor is also used in compounds of the substitute order like textiloid, kerite, etc. Was also the basis of the heevenoid compounds' (which see).

**CANADA BALSAM.**—Sometimes called Canada turpentine. It is derived from the *Abies balsamea*. Specific gravity 0.900-0.998. It is a yellowish or greenish transparent liquid, completely soluble in ether, chloroform, or benzol. It is sometimes called balsam of fir, but it does not really belong to the balsams, being a true turpentine. Strasburg turpentine is sometimes substituted for it commercially. It is used in certain compounds to prevent sulphur from efflorescing. With paraffin, beeswax, and coloring matters, it is used for insulating colored yarns that

are used for annunciator and similar wires, and it was also used by Duncan in gutta-percha cements for leather.

**CANDELITTA WAX.**—This wax is found coating the surface of a plant growing wild in semi-arid northern Mexico and southern Texas. When refined the wax is opaque, of a brownish color. It is intermediate in hardness between beeswax and carnauba wax. Its specific gravity is 0.983. It is used in polishing compositions and for raising the melting point of softer waxes.

**CANDLE TAR.**—The residual products from the distillation of animal fats, oils, etc., are known as candle tar. This product is sometimes soft and ropy, and at other times quite hard. Mixed with sulphur, it is said to produce a compound having some of the elasticity and other desirable qualities of vulcanized india rubber.

**CARNAUBA WAX OR CARN GUM** is found in Brazil, where it forms as a coating on the leaves of a certain palm (*Corypha cerifera*), and is removed by pounding and shaking. It is very hard and is of a greenish or grayish color. Its specific gravity is about 0.995, it is odorless, and melts at 185 degrees F. It dissolves completely in boiling alcohol, and is used on insulated wire as a finish, and in the manufacture of wax varnishes. Used instead of ozocerite as a finish for tape or braids that cover insulated wire.

**CASEIN** (also called Caseum) is one of the chief constituents of milk, being that part which forms the curd of sour milk, and is familiar in the form of cheese. Specific gravity 1.26. A similar substance, prepared from peas, beans, lentils, and the like, is called vegetable casein. It is used in shower-proofing after a German formula in connection with soda, lime, and acetate of alumina; also, in cements of which gutta-percha is the base, for joining small particles of leather, shavings, etc. In Kittel's compound, casein dried and powdered is mixed with linseed oil. India rubber or gutta-percha is then added to the compound. A sample compound is india rubber 10 parts, casein 20, superoxide of lead 10, sulphur 3, and linseed oil 1.

**CERAMYL.**—A material used in the finishing process in the manufacture of elastic web. Its use is to make the web stronger,

and in a measure to act as a size, causing it to lie flat. It is also said to add strength to it. By the application of heat, ceramyl, which comes in the form of a semi-solid, is reduced to a liquid. In English practice this is said to have driven out the use of glue in the dressing of elastic webs. Ceramyl is manufactured in England.

CERASIN, also spelled ceresin, is of a butter-yellow color, odorless, and has a specific gravity of .918 to .922. It is used chiefly in covering annunciator wires where the object is to preserve the colors of the yarns in the braiding. See Ozocerite.

CHERRY GUM.—A pale yellow or red-brown gum, coming from the bark of old cherry trees. It contains 35 per cent. of cerasin, 52 parts of arabicum, and 1 to 3 per cent. of ash. This gum is chiefly used in the manufacture and finishing of fine felt hats. The gums on the market are of two qualities, the German, which is the best, and the Italian. It is used in insulating instead of purified ozocerite, in certain cases where a little more adhesiveness is required.

COALITE PITCH.—A residue of coalite tar, much like natural bitumen and containing little free carbon. An English product.

COAL TAR.—See Tar.

COLOPHANE.—See Rosin.

COLOPHONY.—See Rosin.

COORONGITE.—The name given to a rubber-like mass found in Coorong, South Australia. Some place it among the fossil resins. Coorongite is not soluble in the ordinary solvents used in rubber work, but after mixing with india rubber, it can be put in solution. According to Forster, it vulcanizes somewhat as india rubber does. See Chapter II.

COPAL.—Hard copal is a fossil resin obtained from the East Indies, South America, and the Eastern and Western coasts of Africa. It occurs commercially in roundish, irregular pieces, having a specific gravity of 1.045 to 1.139. It is insoluble in alcohol, partially soluble in ether, and slightly so in oil of turpentine. Soft copal is obtained from living trees in New Zealand, the Philippine Islands, Java, and Sumatra. Used with shellac, asphaltum, and arsenate of potash for waterproofing



leather; also in cements, in proofing compounds, and in varnishes in connection with india rubber, lead, alum, and other ingredients dissolved in spirits of turpentine.

DAMMAR is derived from the Amboyna pine, growing in the Malay peninsula, Sumatra, and Borneo. The resin exudes in tears and is collected after it has dried. It makes a very transparent varnish, the gum being soluble in benzine, essential oils, and to a certain extent in alcohol. Used in artificial leather compounds, and with rubber, asphalt, and fish oil for water-proofing leather. It is quite largely used in rubber cements. Specific gravity 1.10-1.12.

DEXTRINE is an intermediate product between dextrose and starch. Specific gravity 1.04. It is soluble in cold water, and is much used as a substitute for gum arabic in mucilage, as it has strong adhesive properties. Cooley combined it with a little gutta-percha, resin oil, and earthy matters in the production of what he called artificial leather. It is used also in a mixture with plaster of Paris, making a tough surface mold for small experimental rubber work.

DEXTROSE is obtained from starch generally, and is crystallized glucose. Specific gravity 1.39. It is soluble in water, and has many commercial uses. For example, it was used by Hancock as a sizing for cloth on which was spread rubber in solution, the dextrose being there in order to keep the rubber from sticking to the cloth. In other words, this was a sort of cheap calendering process.

EARTH WAX.—See Mineral Wax.

ELASTIC GLUE is used with india rubber and gutta-percha in shoemakers' cements. See Substitutes.

ELATERITE is also known as elastic bitumen or mineral caoutchouc. It appears naturally in soft, flexible masses of a brownish-black color, somewhat resembling india rubber. It is composed of 85.5 per cent. of carbon, and 13.3 per cent. of hydrogen. In its physical characteristics, elaterite is found in infinite variety. It is sometimes elastic and so soft as to adhere to the fingers, and sometimes brittle and hard. One kind of it, when fresh cut, resembles fine cork, both in texture and color, and will rub out pencil marks. Its elasticity is due to its cellular texture, and to

the moisture with which it combines. It is used to a certain extent in insulating compounds, but is intractable and so far shows no special features of value above other minerals of the same series. A few years ago a company was formed in Colorado which claimed to be able to make many kinds of rubber goods from this product alone, but little has been heard of the plan of late. See Gilsonite.

ELEMI comes from the Philippine Islands, and is a resin obtained from certain trees there. It varies from white to gray in color, and is quite soft and very tough. Alcohol and other solvents readily dissolve it, and its office usually is to give toughness to varnishes in which are harder resins. Used in connection with india rubber and benzine in the production of puncture fluids. Specific gravity 1.06.

EUPHORBIVM appears in the market in the shape of tears of irregular shape, varying in size from a small pea to  $1\frac{1}{2}$  inches in length. Of a dirty gray or yellowish color, and very largely mixed with impurities. Must not be confused with *Euphorbia* rubber (which see).

FICHTELIT.—Occurs in a peat bed near Redmitz in the Fichtelgebirge in Germany, and also in fossil pines in the form of scales or flat needles. It has also been met with in Franzenbad and in Denmark. A hydrocarbon little known, though mentioned in certain patented rubber compounds.

FISH GLUE.—Made by boiling the heads, fins, and tails of fish by high heat. Specific gravity 1.27. It is generally made into a liquid glue by a treatment with acetic or hydrochloric acid, whereby its property of gelatinizing is lost. It would have a disagreeable odor were it not for the fact that that is destroyed by adding cerosite or oil of sassafras or something of that kind. Fish glue is used in a cement for cured rubber, in connection with gutta-percha and rubber dissolved in bisulphide of carbon.

FRANKINCENSE.—Also called olibanum (which see).

FRENCH ASPHALTE.—See Auvergne Bitumen.

GAMBOGE.—The best is found in commerce in cylindrical rolls of a dull orange-red color. Another form is that of lumps or cakes. Its powder is bright yellow and its taste very acrid,

but it has no smell. It is derived from a tree which is a native of Cochin China and Siam. Is used chiefly as a pigment. It is the basis of a general cement in which are also found rubber, alum, and burnt sugar, and in another is used with rubber, white lead, gum benzoin, alum, sugar, and sulphur, for cementing vulcanized rubber.

GARNET LAC.—See Shellac.

GILSONITE.—A hydrocarbon valued for its elasticity. Specific gravity 1.10. One of the purest of crude bitumens, it is mined in the Uncompahgre Indian reservation, Utah, United States. It is a black, tarry-looking substance of brilliant luster. It is used for varnish making, in paints, and for insulation, either with or without rubber, one well-known compound consisting of rubber, linseed oil, and gilsonite.

GLUCOSE.—The commercial form is prepared from starch usually, as that is the cheapest raw material. The starch paste being boiled with mineral acids, dextrose, maltose, and dextrine are produced. Glucose in this country is made entirely of corn starch; in Europe, however, sago starch, rice, and potato starch are used. It is neutral, and both odorless and colorless. It is really a kind of sugar that is with difficulty crystallizable, and it is also called grape sugar. It occurs in commerce either as a thick, sweet, heavy liquid, or as a white, solid mass. It is used with rubber, glue, sugar, whiting, and glycerine in making bookbinders' cements, and in making puncture fluids for pneumatic tires. Specific gravity 1.39.

GLUE.—An impure form of gelatin obtained from the horns, hoofs, skins, and bones of animals. Glue of good quality should be bright-brown or brown-yellow in color, free from specks, glossy, perfectly clear, hard, and brittle.

Ground animal glue of ordinary quality has in recent years been employed as a colloidal filler in rubber compounding, particularly in the manufacture of automobile tires and for other purposes where a tough wear-resisting quality is essential. Owing to its nitrogenous composition glue acts as an accelerator in vulcanization. The annual consumption of glue in the American rubber industry totals several million pounds.

GLUGLOSS GELATINE.—A gelatinous product used largely in America in waterproofing fabrics. It is dissolved in hot water

to use, and makes an excellent waterproof sizing. A mixture of glycerine with it increases its elasticity. It combines readily with glue, dextrine, or any such products, and develops considerable adhesiveness.

**GLUTEN.**—A vegetable substance obtained from wheat and other grains. Treated with tannic acid, it is used as a substitute for gutta-percha under a formula by Johnson, who says the product can be vulcanized. Another formula calls for its mixture with oil and sulphur, as a substitute for gutta-percha. In cements it is the basis of one for uniting leather scraps, and is used with a little gutta-percha.

**HELENITE.**—Another name for fossil rubber or elaterite (which see).

**IDRIALIN (IDRIALIT).**—A rare hydrocarbon found in Idria, a province of Austria, where it occurs with hepatic cinnabar. A similar body is obtained in the distillation of amber. Its specific gravity is 1.4 to 1.6. Mentioned in certain rubber formulas to assist the insulating qualities of compounds.

**ISINGLASS.**—A glue substance prepared from the swimming bladders of certain fish. It is white and glistening, occurring in fibers or threads. The best is known as Russian, and comes from Astrachan. Its specific gravity is 1.2. On boiling isinglass it is converted into a very pure form of glue. Isinglass is used in quick-drying cements with india rubber, chloroform being the solvent.

**JELUTONG RESINS.**—Jelutong or Pontianak contains two kinds of resin; one is soluble in acetone—easily in hot, less easily in cold. After acetone extraction Jelutong when submitted further to the action of hot or cold sulphuric ether, or other solvents, yields the second resin, which is insoluble in acetone. Both resins are unsaponifiable and optically active. Their chemical composition is the same but molecular weights different, as are also their melting and boiling points. Probably they are secondary ethylene alcohols near to gum elemi, for which they may serve as substitutes.

Patented solutions of jelutong resin are used as paint thinners and for priming coat on cement surfaces, not being attacked by the cement alkali.

Another and large use is as chief constituent in a composition for coating wire box nails to cause them to hold firmly when driven into wood.

JUNIPER is the gum known as sandarac, obtained from an evergreen growing in northern Africa. It occurs in small, light-colored grains, with a slightly bitter taste. It is soluble in turpentine oil and alcohol. Is used as an assistant in making peroxide substitutes. Mixed with rubber and earthy matters and dissolved in turpentine, it was one of the early compounds for clothing. Its specific gravity is 1.05 to 1.09.

KAURI.—An amber-like substance varying from a soft cream white to an amber color. It comes from New Zealand, and is also known as Australian dammar. The lighter colored kauri comes from living trees, but much of the darker is a fossil resin. It is cheaper than copal and largely used in varnishes. Kauri gum, in connection with rubber gum and pitch, is used for treating yarns used in insulated wire coverings. Parkes added it to rubber goods where the surface was to be printed upon after curing. One pound of sulphur formed Richards's covering for insulated wire. Its specific gravity is 1.05.

LINI.—A gum made from linseed, often used as a substitute for gum arabic. The seeds are first boiled in water for an hour, the resulting thick mass filtered, and then treated with twice its volume of 90 per cent. spirits of wine. A flocculent white precipitate separates, from which the dilute spirit can readily be decanted. The gum is clear, gray-brown, fragile, and dissolves in water. Two grams in 30 grams of oil is almost identical with an emulsion of gum arabic. In connection with coloring matters is the basis for the Knowlton patented waterproofing process.

LITHRO-CARBON.—A kind of asphalt, large deposits of which are found in the state of Texas. It was at one time thought that it would supersede india rubber, and a company was formed with the idea of manufacturing goods from it. This was in 1892, and india rubber is still used. The chemical composition of lithro-carbon is 88.23 carbon, 11.59 hydrogen, .06 oxygen, a trace of sulphur. Lithro-carbon is jet black in color, is flexible



at ordinary temperatures, and is quite tough. Its specific gravity is about 1.028. It is said to be soluble in naphtha, benzol, bisulphide of carbon, etc. It will stand a temperature of 600 degrees F., without giving off its associate products. It resists alkalies and acids, with the exception of concentrated nitric and sulphuric acids. Its manufacture was patented. Used with gutta-percha and shellac it makes an excellent insulator.

MANILA GUM.—See Gum Elemi.

MANJAK.—A kind of asphaltum of which there are extensive deposits in Trinidad, West Indies. Used chiefly in varnishes.

MASTIC.—A resin from the shores of the Mediterranean. It occurs in tears of a pale yellow, is brittle, and of a faint balsamic odor. Specific gravity 1.07. It dissolves in acetone, turpentine oil, and alcohol, and is largely used in varnish. The residue obtained in the purifying of mineral asphalt is also called mastic. It is used in general rubber cements for joining stoneware, earthenware, leather, etc. One of special value calls for 10 parts of mastic to 1 part of india rubber, dissolved in chloroform, and makes an excellent cement for fastening letters to glass. The gum also appears in many old-fashioned compounds.

MENTHOL is obtained from the oil of peppermint coming from Japan and China, or from the oil of spearmint manufactured in the United States. Its melting point is about 108 degrees to 110 degrees F., and it is slightly soluble in water, but freely in alcohol. It is often used in medicinal plasters which have rubber for a base.

MINERAL INDIA RUBBER ASPHALT is the name of a material composed of refuse tar produced during the refining process of tar by sulphuric acid. It is black, like ordinary asphalt, and quite elastic. It is an excellent non-conductor of electricity, and is not assailed by acids or alkalies. In a naphtha solution, it yields a waterproof varnish for metallic objects, and is used in rubber compounding in place of asphalt.

MINERAL TALLOW, also called hatchetine, is a substance found in Siberia, Germany, and Great Britain. It is an earth

wax that is soft, flexible, and runs from yellow to yellowish white. It has no smell, and melts at from 115 degrees to 170 degrees F. It is composed of 14 parts hydrogen and 86 carbon. Mineral tallow is used sometimes in place of earth waxes in insulated wire work, and has been used in paste blackings in connection with india rubber.

**MINERAL WAX.**—A term applied to several waxy-looking hydrocarbons found as mineral deposits, such as neft-gil, ozocerite, montan, and earth wax. It is found in Austria, and in the southern part of Russia, on the shores of the Caspian sea. In the United States it occurs largely in Texas and Utah. Used chiefly in insulating compounds. See Ozocerite.

**MYRRH** exudes from the bark of a tree which grows in Arabia, in yellow drops that are quite oily at first, but which thicken and become hard and of a dark color. It appears in commerce in either grains, or tears, or in pieces of various sizes and irregular form, the color being red, reddish-brown, or yellow. Its taste is bitter and aromatic, and its smell balsamic. The best gum is known as Turkey myrrh. It is used with rubber, sulphur, and salicylic acid in complexion masks. Specific gravity 1.36.

**NATURAL PITCH** is the name given to such kinds of pitch as are not manufactured, such as asphalt, bitumen, etc.—that is, pitch of a mineral origin, except that from coal or shale. See Asphalt.

**OLEO RESINS.**—A resin that contains a certain amount of the essential oil of the plant from which it exudes is so called. Chief among the oleo resins are certain which have a pungent taste and a peculiar, and often a pleasant odor, known as balsams.

**OLIBANUM.**—The frankincense of the ancients, obtained chiefly from Asia and Africa. Specific gravity 0.863. It occurs in yellowish, somewhat translucent tears, with a balsam-like resinous smell, and an acrid aromatic taste. Sometimes called gum thus. It is largely used in the manufacture of porous plasters.

**OZOCERINE** is a vaseline-like substance prepared from ozocerite. There is also prepared from crude ozocerite a valuable

black wax which, when mixed with india rubber, makes an excellent electric insulating material. This wax was recognized by a lecturer before the Society of Chemical Industry as the basis of the insulation known as *okonite*.

**OZOCERITE.**—A waxy hydrocarbon occurring in Austria, southern Russia, and the United States. It is also known as *earth wax*. Its specific gravity is 0.9 to 0.95, and it is about as hard as talc. Chemically, it consists of hydrogen 13.75 and carbon 86.25, while its melting point extends from 140 degrees to 170 degrees F. It is often found adulterated with asphalt and sometimes with Burgundy pitch. Purified ozocerite is known as *cerasin*. To make this, the crude material is treated with fuming sulphuric acid, and then filtered through charcoal. Thus prepared it is of a pale yellow color, the melting point ranging from 61 degrees to 78 degrees C. It has almost wholly driven out Stockholm tar as a protection for wires insulated with gutta-percha, when placed under ground. It improves the insulation, but in spite of common belief to the contrary, does not preserve textile fabrics. The best compound for the protection of the insulation on wire consists of 3 parts ozocerite to 1 part of Stockholm tar. It is an insulator of high quality, and while it is in some ways intractable, its wax-like nature allows it to combine with other insulators or with textiles. It is also used as a water-repellent in fabrics, the gum being volatilized by heat, and the fumes passed through the cloth. As a surface covering for tapes or braids, it is often employed and is better than other gums, as it takes a fine polish from the polishing machine. The basis of Henley's system of curing india rubber core is melted ozocerite, which is used under pressure to remove all the moisture, being afterward heated in hot ozocerite, which stops up the pores. Ozocerite, mixed with india rubber, is also the basis of the india rubber compound called *nigrite*. It mixes, however, with difficulty with india rubber, which is an objection to many proposed uses of it. It also has a mildly deleterious effect on it.

**PARAFFIN.**—A white waxy-looking body obtained from petroleum and certain tars by distillation. It is tasteless, inodorous, harder than tallow, but softer than wax. Its specific

gravity is .877. It is also obtained from ozocerite or earth wax. Its melting point varies with the source it is obtained from. It is insoluble in water and nearly so in boiling alcohol, but soluble in ether, oil of turpentine, oil of olives, benzol, and bisulphide of carbon. It is usually very free from water, and not liable to absorb it. It has been used as a waterproofing mixture and is a good insulator. When gossamer clothing was manufactured in large quantities, the surface of the goods before solarization was covered with a thin coat of paraffin, which gave it a peculiar shade until the solarization was completed, when all traces of the paraffin seemed to disappear. The insulating capacity of rubber to which paraffin has been added is quite remarkable, but at the same time it lessens the hardness of the rubber to a marked degree. Rubber dissolved in paraffin wax forms a curious compound which has been used in insulation. Paraffin is used in the artificial gums, like parkesine and insulite; also with cottonseed oil and resin for cheap brattice cloth, and in cheap proofing compounds. It is not a great favorite as an insulator, as it shrinks in cooling, causing cracks. Paraffin tapes are also easily destroyed through the presence of free acid. It was formerly used largely in covering annunciator wires, but as it was found to absorb and retain water, its use was given up, and its place was taken by a compound of paraffin, cerasin, and resin. It is used in some rubber compositions for tubing-machine work to render the stock smooth running and give a fine finish.

PITCH is the black residue that remains after the distilling of wood tar. Varieties are also obtained from coal tar and from bone tar. Wood pitch, however, has a toughness which the others do not possess. Specific gravity 1.07-1.10. Pitch was used very early in considerable quantities in hard-rubber compounds. Goodyear, for example, used considerable of it in hard compounds for coating metal, the rest of the compound consisting chiefly of rubber and sulphur. It is almost the only organic substance which largely increases the resiliency of india rubber. It is largely used in cements, and also in many rubber compounds. Equal parts of pitch and gutta-percha make a tire cement for fastening to the rims, known as "Davy's Universal Cement." It is used with gutta-percha in shoemakers' wax, and

also in certain proofing compounds. Wood cements made of gutta-percha as a rule contain a certain amount of pitch. It is also used in the manufacture of Fenton's artificial rubber.

**RESINS.**—The term given to a number of complex bodies, generally the hardened exudation of sap from trees. Chemically a resin is the substance obtained by the gradual oxidation of an essential oil. The specific gravity ranges between 1.02 and 1.2. Resins are divided, as a rule, into three classes—hard, soft and gum resins. The former at ordinary temperatures are solid and quite brittle. They contain little or no essential oil, and are easily pulverized. Shellac and sandarac are good examples of this kind, and soft resins are usually called balsams, and are either semi-fluid, or soft enough to be molded by hand. They are really mixtures of hard resins, and the essential oils found in the plant from which they come. On exposure to the air they become in time hard resins. Of this class are balsam of storax, tolu balsam, etc. Gum resins are the solidified milky juices of certain plants. They consist of a mixture of resins, essential oils, and a considerable proportion of gum. These are, for example, gum euphorbium, galbanum, and to this class also belong india rubber and gutta-percha. Most of the fossil gums, such as copal, are resins whose physical characteristics have been changed by their having been buried for a long time in the earth. These fossil resins are counterfeited to an extent by treating ordinary resin with lime, which raises its melting point considerably.

**RETINITE.**—Also known as retin asphalt. It is a fossil resin found in brown coal. It is found in roundish masses of a yellow-brown or reddish color, is quite inflammable and readily dissolves in alcohol. At present it is somewhat rare, but if it ever should become common, it would undoubtedly find a place in rubber compounding. Its specific gravity is 1.07 to 1.35.

**ROSIN** is made from common turpentine, which is distilled in water, yielding nearly one-fourth its weight of essential oil, the residue in the retort consisting of common rosin. Rosin is also very generally called colophony, its true chemical name distinguishing it from the other resins. There are two varieties of rosin in common use, the brown and the white. The first



named is brittle, solid, and of an amber color, and comes from the Norway spruce fir. The white rosin is obtained from the pine and is known as galipot. Rosin dissolves very freely in alkaline solutions, which allows of its use in soaps. Its specific gravity is 1.08. There are three grades commonly on the market, which are called virgin, yellow dip, and hard. It is used in a great variety of rubber compounds, its chief uses being in frictions, dry heat varnishes, cements, and the puncture fluids. Almost all lines of rubber manufacture use a certain amount of it at times. Only a small proportion of it can be used in rubber compounding, its office being usually that of the sticker. A large amount of it induces surface cracking, and often a decided blooming of the sulphur. It is also used in waterproof solutions in conjunction with spermaceti, india rubber, and paraffin wax. Mixed with boiling oil, it has been applied to gutta-percha articles to give them a Japan-like luster, and is also important in gutta-percha glue, which is compounded of gutta-percha, powdered glass, litharge, and rosin. A very large use for it is in the rubber channel cements that are sold to leather shoe manufacturers.

SANDARAC.—Also known as Gum Juniper (which see).

SEEDLAC.—See Shellac.

SENEGAL.—See Arabic.

SHELLAC, STICKLAC, SEEDLAC, LAC.—All these are different names for the same thing or different stages of its preparation. It is the exudation formed on several sorts of trees growing in the East Indies, but is chiefly produced from the banyan tree, the exudation coming from a scale-shaped insect known as the *Coccus lacca*, the female fixing herself to the bark and exuding the resinous substance from her body. In addition to the East Indian product there is what is known as Mexican lac, which exudes from the *Croton draco*. Sticklac is the resin as taken from the tree. Seedlac consists of fragments broken from the twigs and partly exhausted by water. Shellac is prepared by melting stick or seedlac, straining, and pouring upon a flat surface to harden. It is then washed, dried, melted, roughly refined,

and sent to market, or it is poured into molds to harden and is known as button or garnet lac. The specific gravity of lac is about 1.139. It is partially soluble in alcohol, turpentine, chloroform, and ether, and is completely soluble in caustic alkalies and borax solutions. Shellac was formerly used very generally in rubber manufacture in surface goods, and particularly in solarized goods in small proportions. It has a specific use to-day in the production of water varnishes for surface goods. It is also a constituent in the production of certain compounds in hard rubber, and particularly the semi-hard varieties, being used to the extent of 20 per cent. of the amount of gum. Although quite brittle, it seems to impart a certain elasticity to the product. The maximum use of shellac in a hard-rubber compound, according to Hoffer, is 88 parts india rubber, 50 parts shellac, and 12 parts sulphur. It is also used in certain of the Jenkins patented packings to the extent of 10 to 25 per cent. of the amount of rubber, where it is said to preserve the compound from the effects of coal oil, steam, or hot water. It is also used in many cements both with and without india rubber, one formula for marine glue being: 20 parts shellac, 12 parts benzol, and 1 part india rubber, mixed with heat. Dissolved in 10 parts of strong aqua-ammonia, it forms a varnish for rubber goods, and is also used as a solution for re-varnishing old rubber shoes. Used with carburet of iron and bisulphide of mercury as a cement for card clothing, with india rubber and gutta-percha for attaching shoes to horses, in English "ale cement," and in certain proofing compounds.

SIZE.—A weak solution of glue, sometimes used in shower-proof compounds and cements. The name size is also often applied to any thin viscous substance, as for instance, gilders' varnish. In rubber practice, however, the glue is what is ordinarily employed. It is also used in preparing a perfectly smooth cloth upon which rubber is to be calendered, and from which it is stripped before the making up. See Glue and Gelatine.

SLUDGE OIL RESIN.—A heavy, gummy residue from the waste of superphosphate factories. Has been used with rubber in making Japan varnishes.

SPRUCE GUM is used with chicle in the production of chewing gums.

STEARINE.—A white waxy-looking body obtained from fats—chiefly tallow and palm oil. When made from tallow it is called pressed tallow or tallow stearine, which is the solid part obtained from the heating of suet fat and the removal of the liquid part, which is oleomargarine. Tallow stearine is very largely used in candle making, where is found saponified stearine, distilled stearine, and distilled grease stearine. The usual specific gravity of stearine is .920. This latter contains considerable cholestrol and differs from commercial stearic acid or stearine chiefly in its physical structure. Stearine is used in proofing compounds, in rubber blackings and in compounds containing resins. It has been suggested that a small proportion of stearine in certain rubber compounds that contain low grades of rubber, which in themselves have large proportions of resin, has a decided value in preventing oxidization.

STEARINE PITCH.—The brown, tarry residue left in the still during the process of refining tallow and fat. Used in the manufacture of certain packings that contain no rubber. Stearine pitch is also used as a lubricant for bearings that have a tendency to heat.

STICKLAC.—See Shellac.

STOCKHOLM TAR is used in black cements of the marine glue class, and is also used in rubber compounding, its office being to assist in the mixing of dry compounds, and as a binding material for sulphur in the dry-heat cure. Also used in manganese cements and in cements to fasten tiles to floors.

SPERMACETI.—A peculiar fatty concrete substance obtained from the head of the sperm whale. Its specific gravity is 0.943, and it is fusible at 112 degrees F. Insoluble in water, soluble in hot alcohol, ether, and oil of turpentine, but redeposited as the liquids cool. Was formerly used in certain waterproofing compositions.

TAR.—This substance is derived from the animal, vegetable, and mineral kingdoms. From the first, by the destructive dis-

tillation of bones, is produced what is known as "Dippel's oil"; from the second, by the distillation of pine woods, the product is known as pine tar or Stockholm tar; and from the third, by the distillation of coal, is produced coal tar. Of the three, coal tar is the most used in rubber work, its office being to help carry adulterants in dry mixing and to keep the sulphur from blooming after vulcanization. It is used chiefly in dry-heat work. Goodyear discovered early that very large quantities of boiled tar could be used in connection with india rubber and sulphur without injuring the quality of the gum, and it has been very generally used since his time.

THUS.—A name for gum turpentine, and rarely for olibanum. Used with rubber and japan for waterproofing leather.

TOLU BALSAM is derived from a tree found on the mountains of Tolu, and the banks of the Magdalena river, in Colombia. It is very similar to balsam of Peru. It sometimes appears in commerce in dry friable fragments, the newly imported gum being soft and tenacious. It is very fragrant and has a medicinal and tonic effect. Tolu balsam is used with paraffin wax and chicle in chewing gum compounds.

TRAGACANTH is an exudation which comes in the form of translucent plates of a dull white, which water swells and partly dissolves. It is often used in mucilage in place of gum arabic. The gum comes from the Levant from the *Astragalus gummifera*. Has been used in connection with gutta-percha for making dental plates that are soft and adhesive to the membranes and that will not rot or deteriorate.

TRAGASOL.—This is a gum produced from the kernels of the *Ceratonia siliqua*. The use of this gum as a solvent for india rubber, gutta-percha, or celluloid has been patented in England. A mixture of 25 parts of dissolved india rubber, 75 parts of strong gum solution, with the addition of 1 part of carbolic acid to 500 parts of the mixture, makes a cement for wood, and a preservative paint against insects and vermin.

TRINIDAD ASPHALT is obtained from the pitch lakes of the island of Trinidad. Its specific gravity is 1.2, and it is somewhat soluble in alcohol, while Persian naphtha, oil of turpentine, benzol, and benzoline readily dissolve it. See Asphalt.

TURPENTINE.—This is a semi-solid resin, which comes from various species of pine as a rule. The chief commercial varieties are common turpentine, which comes from the *Pinus palustris*; Venice turpentine, from the larch; Bordeaux turpentine, from the *Pinus maritima*, and China turpentine, from the *Pistacia lentiscus*. Of these the Venice turpentine is said to be the best. It is of a pale yellow color, transparent, has a bitter taste, but a balsamic odor. Used instead of rosin in many compounds. Specific gravity about .90.

VEGETABLE PITCH.—The residue left after distilling the tar made from wood of various trees. Called vegetable to distinguish it from the mineral pitch, which is derived from coal. See Pitch.

XANTHORRHŒA GUM is somewhat similar to shellac, is abundantly produced in the Australian colonies, and sometimes used in the compounding of ebonite. Zanthorrhœa gum is also sometimes known as gum acroides, and is produced from the Australian grass tree. See Acroides Gum.

XYLOIDIN.—An artificial gum much resembling pyroxylin obtained by the action of nitric acid on starch.

XYLONITE OR ZYLONITE.—See Celluloid.



## CHAPTER X.

### PIGMENTS USED IN COLORING INDIA RUBBER.

MOST of the india rubber goods now manufactured are black, this color, if it may be so called, being produced in a measure by the color of the rubber, together with the leads and other ingredients, most of which darken during vulcanization. The next prominent color, from a rubber standpoint, is white, produced by either an oxide or sulphide of zinc. Next to this range the yellows and reds, produced by the sulphide of antimony, vermilion, and oxide of iron.

So many colors are unstable when brought in contact with sulphur during the heat of vulcanization, and it is so difficult to get good effects, that it is hardly to be expected that beautiful colors in india rubber will ever become common. There are various methods used for changing the natural color of india rubber. The usual way is by incorporating, by mechanical mixture, earthy pigments or metallic oxides or sulphides, or vegetable coloring matters, which, by their covering property and strength, give to the india rubber their own particular shade. There are other methods, however. For example, there have been produced anilines soluble in benzine, that are used for surface work, such coloring being really an elastic enamel. Toys and minor articles that are ornamented in very bright colors, however, are generally painted over after vulcanization, but paint is not durable, nor does it long remain beautiful.

While it is claimed ordinarily that it is impossible to dye india rubber, it should be remembered that the attractive colors that appear on children's toy balloons and similar pure-gum goods are applied as dyes, the colors being anilines, with methyl alcohol as a vehicle. These colors are boiled in rainwater, and when the solution is cold the balloons are put into the coloring liquid and turned so as to have their entire surface wetted. After that, they are dropped into cold water, which washes off

the superfluous color. When this is done properly, the rubber does not give off any stain at all after the first washing. The colors used in this way are red, green, blue, orange, and pink, but other shades are equally available.

Germany produced a full line of aniline colors soluble in benzine and for surface coloring of rubber goods they have been found very valuable. Although they are not absolutely fast, they are sufficiently so for all practical purposes. In many cases, these aniline colors, being soluble in benzine, can be mixed with india rubber—that is, when it is used in the form of solution. If the product be cured in open steam heat with sulphur, some very curious effects are likely to be obtained. This was proved at one time when a line of rubber colors was put on the market in the United States, with white oxide of antimony as a base, and anilines to give various shades. It does not often happen, however, that a problem of this kind confronts the users of aniline colors in rubber, the more general and sensible way being that of surface coloring. This is done in some cases by simply brushing the aniline color dissolved in benzine over the surface of the article. It is desirable, however, first to dip the goods in the dissolved mordant, and then to use the brush, if necessary. Where a high polish or a polished effect is desired, some sort of elastic lacquer must be put on over the coloring matter. A very thin india rubber solution is often used for this.

In speaking of anilines, it must be remembered that those that have to be worked up with acids should be avoided for rubber work, but there are so many others that there is no need of the rubber man making this mistake. Where colors are to be printed upon rubber surfaces, a little dextrine is added to the aniline dissolved in benzine, and to make the color dry faster, a little sulphate of manganese mixed with half of one per cent. of alum and added to the mass is advisable.

Black, blue, red, yellow and green anilines are also used in coloring rubber cements that go to the leather shoe trade. These and other anilines are also used very generally in artificial leather compounds. Aniline black is used in water varnishes for luster coats and blankets.

It is also a good idea to sponge the rubber surface with a water solution of alum before the color is applied. The use of alum as a mordant may be supplanted by bisulphate of soda, if it is desired. The best colors available in the aniline series are reds, particularly magenta reds, and the marine and alkali blues.

A great many methods of surface coloring have been devised, some of them being ludicrous attempts at dyeing rubber. The surface of rubber is, of course, not easily affected by colors, unless it has first been attacked and roughened by some powerful solvent. Malcolms' process for this surface coloring is perhaps as harmless as any. This method is to expose the rubber to the sunlight while it is immersed in alcohol. When the surface is somewhat disintegrated, the rubber is taken out, washed, and dipped in a dye solution.

The colors that follow are described very briefly, and any rubber manufacturer can easily secure most of them for use or for experiment.

#### BLACK.

THERE are more methods of getting black rubbers than almost any other color, as the tendency of the gum itself is to darken under heat and the action of sulphur, and the sulphides of most materials that are used in the compounding have the same effect. Most rubber goods are made up without regard to color, and are usually a dirty brownish-black, tempered by the yellow of the sulphur bloom. Where a genuine black is wanted, lampblack is one of the most common ingredients used.

**BLACK HYPO.**—This is also known as hyposulphite of lead. It is really a mixture of thiosulphate of sodium mixed with acetate of lead, and appears as a fine white crystalline precipitate, which should be called thiosulphate of lead. There are two forms, the white hypo and the black hypo, the difference being that the white when heated is transformed into a soft black powder containing very little free sulphur. The black of the compound being sulphide of lead often contains over 90 per cent. of pure sulphide. It is an excellent vulcanizing

agent, and also a filler. When properly prepared it makes goods absolutely free from bloom.

**BONE BLACK** (animal charcoatl), sometimes called ivory black, is a black powder obtained by grinding the product of bones that are burned at a red heat in close vessels. It is more dense and less combustible than lampblack. A good quality should have an even color, of a rather dull shade. The carbon content of bone black varies from 10 to 20 per cent., the rest being principally calcium phosphate combined with moisture and small amounts of impurities. Its specific gravity is 2.82-2.86.

**CARBON BLACK** is the trade name given to lampblack made upon the surfaces of metal or stone by direct impact of flame, from which the black is removed by scrapers. Specific gravity 1.73. The fuel employed is natural gas. Carbon black is much more intense in coloring effect than any other form of lampblack and is preferred for rubber compounding.

Other trade designations for carbon black are hydrocarbon black, gas black, satin-gloss black, jet black, silicate of carbon, Paris black, etc.

**GAS BLACK.**—See Carbon Black.

**GRAPHITE BLACKS** of late have been used very largely in rubber compounding and have done excellent work. They are not as black as the better grades of lampblack made from oils or resin. They are in many cases wholly inert, however, and therefore perfectly safe to use. One of the best types of this sort of coloring matter comes from a graphite mine in the United States. It is wholly amorphous, and has none of the flaky make-up that ordinary graphite has, but is 97 per cent. pure carbon. These blacks are said to give a brighter finish to varnished goods than ordinary lampblacks. The specific gravity of graphite varies from 2.17 to 2.32.

**HYDROCARBON BLACK.**—See Carbon Black.

**JET BLACK.**—See Carbon Black.

**LAMPBLACK.**—Lampblack, however, is carbon in its amorphous or spongy form. Specific gravity 1.68-1.70. It is ob-

tained on a large scale by collecting the smoke produced during the combustion of oils, fats, resins, coal, gas, tar, wood tar, petroleum residues, dead oil, and even bituminous coal. This accounts for the various grades that are to be found on the market. Large quantities of lampblack are manufactured from natural gas and known as carbon or gas black. There are many types of lampblack, the best in the world being employed in the preparation of india ink. This is made from burning camphor, a lower grade being made from the mixture of camphor and other oils. The smoke is collected on leaves, washed, dried, and sifted with the utmost care.

The lines of rubber goods in which lampblacks are generally found are rubber boots and shoes, black automobile treads, surface clothing, and carriage cloth, druggists' sundries (where the leads are deemed dangerous), and in certain compositions where emery is the chief ingredient used for grinding or polishing. A curious fact about lampblack is that a little bit of it in unvulcanized rubber seems to assist the erasive quality, and does not cause smutting. A little of it is also sometimes added to churning mixtures that do not readily mix.

**LEAD SULPHIDE.**—This is a valuable coloring matter for rubber, as it gives a good black, besides which it makes goods exceedingly resilient. There are great differences in the production of lead sulphides, but a good one is of special value to rubber manufacturers. Specific gravity 7.13-7.70.

**PARIS BLACK.**—See Carbon Black.

**SATIN GLOSS BLACK.**—See Carbon Black.

**SILICATE OF CARBON.**—See Carbon Black.

**URANIUM SULPHIDE.**—A fine black pigment more intense than plumbic blacks. It is a permanent color, and is said to be a preservative of rubber.

#### BLUE.

**BLUES** are not largely used in general rubber work. They are found chiefly in toys, in sheetings, and in certain packings.



CHROME BLUE is manufactured from silica, fluor-spar, and chromate of potash. The resultant material is a deep blue vitreous mass which is reduced to an impalpable powder. It is less sensitive to acids than ultramarine, and is better adapted for rubber goods.

COBALT BLUE is manufactured from oxide of cobalt, phosphate of cobalt, and alumina. It is rarely used in coloring rubber where the ingredients are to be mixed with the mass, ultramarine being much superior. Also called smalts.

INDIGO BLUE is prepared from plants of the *Indigofera* genus. Pure indigo is insoluble in water, nor is it soluble in weak acids or alkalies. A small percentage is dissolved in alcohol and its solution is more considerable in turpentine. Indigo blue for rubber is said to be valuable on account of its preserving qualities, which are double those of other blues. Its specific gravity is 1.35.

MOLYBDENUM BLUE.—A pigment recommended by Lascelles-Scott is a bisulphide of molybdenum. It is an exceedingly beautiful blue, but costly. Large new deposits of this mineral have been found in the United States and Australia, and Norway, and it is likely to be so cheapened that it will be a valuable rubber pigment.

PRUSSIAN BLUE (known also as Chinese blue).—A dark, brilliant blue compound, having iron for a base. There is a soluble and an insoluble variety of this compound which is of a somewhat complex chemical constitution. Heated strongly in the air, the insoluble form of Prussian blue burns like tinder. When boiled with caustic potash, it is decomposed. If the dry powder be strongly rubbed in a mortar, it assumes a copper-red luster. In commerce it occurs in irregular shaped masses, having a characteristic conchoidal fracture and copper-red luster.

SAXON BLUE is the original name of the pigment known to-day as smalts; it was also very frequently called enamel blue. Under this name was also sold a blue pigment made by mixing Prussian blue with alumina or a white clay.

SMALTS.—This is what may be called a deep tinted cobalt glass. The analysis of smalts of good quality is as follows:

	Deep- Colored Norwegian	Pale- Colored German
Silica .....	70.9	72.1
Potassa (with traces of soda and lime).....	20.4	20.0
Oxide of cobalt .....	6.5	2.0
Alumina .....	.4	1.8
Peroxide of iron .....	.3	1.4
Other earths and oxides, and loss.....	1.5	2.7
Total .....	100.0	100.0

This is one of the few colors that are practically indestructible. In using smalts for the pigment, large quantities are necessary, as the color is not strong.

THENARD'S BLUE is similar to cobalt blue, but is a more beautiful pigment. It is used chiefly as a surface color. White pigments in small quantities added to this blue make beautiful turquoise colors.

ULTRAMARINE.—This is the most important blue used in rubber. Its composition is essentially the same whether genuine *lapis lazuli* or artificial. Artificial ultramarine is equal and often superior to the natural pigment. This is made of kaolin, carbonate of sodium, willow charcoal, and sulphur. The following analysis of the natural ultramarine is given:

Silica .....	37.6
Alumina .....	27.4
Sulphur .....	14.2
Soda .....	20.0

Analyses of the best artificial ultramarines show these figures:

Silica .....	40.25	39.39	40.19
Alumina .....	26.62	24.40	25.85
Sulphur .....	13.42	12.69	13.27
Soda .....	19.89	21.52	20.69

Ultramarine appears in commerce as a fine blue powder of various standards of fineness. Acids readily destroy it, but alkalis have no effect on it. It stands heat well, not changing below a low red. It is used in cements for backs of memorandum blocks, and in blue soft rubber goods, particularly in vapor-cured goods, such as sheeting. When mixed with chrome yellow it makes a green; with colcothar, it makes a violet.

Mixed with rose pink, oxide of zinc, and Indian red, it produced the well-known wine-colored coat that was so popular a few years ago. It is claimed that ultramarine blue keeps rubber from overcuring, and that it is, therefore, a most useful ingredient to add to compounds that are exposed to heat. A very little ultramarine blue added to a black in rubber sometimes overcomes the grayish shade. A small amount of blue added to white dispels any yellowish tint and consequently improves the whiteness of the goods.

**YALE BLUE.**—In certain soft rubber goods, where a strong blue is needed, ordinary ultramarine was found unsatisfactory. A firm of rubber chemists therefore produced Yale blue, which is a strong coloring matter, and wholly inert as far as the rubber is concerned. Yale blue is an ultramarine entirely free of alum and gypsum.

#### GREEN.

It is fortunate that greens are not largely sought in the rubber industry, for they are rare. Arsenic greens in many cases are not to be thought of; therefore, about the only ones that are available, unless very high cost goods can be utilized, are the following:

**CHROME GREEN.**—A coloring matter that is not affected by strong acids, or alkalies, and which is inert when mixed with india rubber. Specific gravity 4.91. It is the best mineral green that can be used in connection with rubber. It is really a sesquioxide of chromium; and may be mixed with rubber, with any kind of solvent, and with other oxides and pigments, without hurt to the compounds.

**HUNGARIAN GREEN** is a similar pigment found at Kernhausen in Hungary. These greens in some respects resemble the article now known as terra-verte.

**SAXON GREEN** is a green earth of a clayey nature, found in parts of Saxony. Its specific gravity is 5.04.

**TERRA-VERTE** is of mineral origin, and is imported in large quantities from Italy. It is a pale neutral green of moderate cost, and is not injurious to rubber. On analysis it shows, as

in the following table, the chemists quoted being Klaproth for No. 1 and Berthier for No. 2:

	No. 1	No. 2
Silica .....	51.50	46.00
Alumina .....	12.00	11.70
Protoxide of iron .....	17.00	17.40
Lime .....	2.50	3.00
Magnesia .....	3.50	8.00
Soda .....	4.50	.....
Water .....	9.00	13.90

ULTRAMARINE GREEN is made by a process very similar to that made in producing blue of that name, and its action upon rubber is almost identical with that of ultramarine blues.

#### RED AND BROWN.

THE strong red coloring matters used in hard rubber work are mostly of a mercurial base. These are vermilion, red chromate of mercury, sulphide of mercury, and iodide of mercury. The Chinese vermilion, which is the best, is prepared by a special process of their own, and contains 89 per cent. of pure mercury, the rest being sulphur. This coloring matter is used very largely in dental vulcanite, small amounts of it also giving excellent shades in soft rubber goods. Cinnabar and Paris red are also mercurial sulphides, and very strong colors. The sulphides of mercury are really the only ones that are safe and valuable for producing these colors. Red chalk and natural clay containing a certain amount of iron are used chiefly as fillers in rubber goods, although a certain quantity of them produces a dark red color.

ANTIMONY CRIMSON SULPHIDE.—This is altogether the best antimony color now in use. It gives a fine shade of orange or red. Specific gravity 4.20.

COLCOTHAR.—A form of oxide of iron of specific gravity 4.8 to 5.3. It is the acid free calcined residue of iron pyrites from the manufacture of sulphuric acid. The least calcined portions, scarlet in color, are termed jewelers' rouge, and the more calcined parts, of bluish shade, are called crocus. Its composition is ferric oxide. In its reaction it is indifferent, being very stable under ordinary conditions. Colcothar is a dull red and is often used in red packings, solings, etc.

HEMATITE.—An ore of iron, somewhat soft and friable. Specific gravity 5.19 to 5.28. Composition 70 per cent. iron, 30 per cent. oxygen. Insoluble in water, alcohol, or rubber solvents. As a colorant in rubber work it is unchangeable chemically. Used in packings and for red maroons.

INDIAN RED.—A deep rich iron oxide red, made in different shades and purities.

IRON OXIDE.—Pure bright iron oxide, made by calcining iron sulphate. It contains 96 to 98 per cent. of iron sesquioxide, the remainder being silica. The cheaper grades sometimes contain water of crystallization. The better grades are prepared by wet grinding in buhr and pebble mills. See Colcothar.

IRON PEROXIDE.—An old name for the sesquioxide of iron.

ORANGE VERMILION, crystalline lead chromate, gives a very handsome color in connection with rubber, but is rarely used, as it is not permanent if other metals, such as copper, brass, iron, and zinc, come in contact with it. Specific gravity 6.12.

OXIMONY.—A special brand of red oxide of iron for the rubber trade. It has about four times the color strength of sulphuret of antimony.

PRINCE'S METALLIC PAINT.—An impure oxide of iron of variable analysis containing much silica and alumina.

PRUSSIAN RED is an oxide of iron prepared from copperas, and, therefore, it is the same as the modern rouge or oxide of iron.

RED OCHER.—An impure oxide of iron. A dull-red earthy substance containing clayey matter, and having a specific gravity of about 5.2. Used chiefly as a filler, as the color is not strong. As far back as the time of Dr. Mattson, red ocher, Venetian red, and Indian red, were advised by him for use in rubber compounding. Indeed, he obtained a patent for packing in which Venetian red was the principal adulterant.

VENETIAN RED.—The usual composition of Venetian red is a combination of ferric oxide and calcium sulphate in the proportion of 20 to 40 per cent. of the former to 60 to 80 of



the latter. It is made in the dry way by heating ferrous sulphate with lime. It is inferior in pigment effect to ordinary iron oxide. The color is dull brick-red.

VERMILION.—The red form of mercuric sulphide is a scarlet red powder of specific gravity 8.12. It is sometimes adulterated with red lead or red oxide of iron, but such adulterations can be detected by heating a small sample of the suspected article on a porcelain or platinum dish. If any adulterant is present it will remain behind as a residue, since pure vermilion is completely volatile. This substance is sometimes called cinnabar. A substitute for vermilion in hard rubber was brought out by John Haliday in 1870. This was a mixture of garancine and cochineal, in water solutions, boiled and mixed in the proportion of 5 parts of garancine liquor to 1 part of cochineal liquor. To each gallon of this compound liquor 2 pounds of pure oxide of antimony were added; then heating until the water was evaporated and the new coloring matter perfectly dry. Another vermilion substitute was antimony crimson sulphide. According to A. D. Schlesinger, veteran hard rubber expert, antimony crimson sulphide, when mixed with india rubber and sulphur, will, during vulcanization, impart to hard rubber a light red color very similar to that obtained by the use of vermilion. The proportion of sulphur is the same as is used ordinarily in making vulcanite, while to each pound of rubber are added 12 ounces of crimson sulphide of antimony.

#### WHITE.

ONLY a few colors are available for use in making white rubber goods. Of these, the zincs take the lead, being by far the most constant and valuable. They lend their color to the mass simply by their presence as dry paints with strong coloring qualities.

BARIUM WHITE.—This is also called constant white, or *blanc fixe*, and comes from the sulphate of barium or heavy spar. In treatment, it is ground very fine, treated with hot hydrochloric acid, washed, dried, sifted, and then forms a fairly white, dense, impalpable powder. Artificial barium sulphate or

*blanc fixe* is obtained by precipitation from a solution of barium chloride with a solution of sulphate of soda. It is identical with the mineral barytes in all of its chemical properties. It is a brilliant white of exceedingly fine grain. It is highly esteemed in rubber compounding and has a specific gravity of 4.20. This is somewhat less than the specific gravity of natural barytes. It is one of the few metallic colors that the German anti-poison act allows manufacturers to use in any way they please. See Barytes.

BECKTON WHITE.—See Lithopone.

BORATE OF ZINC.—A zinc salt, precipitated by 20 to 30 per cent. of a soluble borate, the result being a white powder, which is claimed to have a distinctively preservative influence when used in rubber, while the tensile strength of the gum is much enhanced.

BOUGIVAL WHITE was a fairly common white pigment, although it has been replaced by barytes, terra alba, and whitening. Bougival white is a white, marly, China clay found at Bougival, near Marly, in France. The district surrounding Bougival and also Normandy and Auvergne contains many beds of white clays, notable for their smooth qualities of good color. Roughly Bougival white contains 33 per cent. chalk (carbonate of lime) and 67 per cent. kaolin (hydrated silicate of aluminum).

CALAMINE WHITE.—This is prepared from the native carbonate of zinc, by calcining and grinding. It is not a strong white, and is not nearly as good as the oxide or carbonate of zinc as a coloring matter. For a cheap white, and a filler, however, it is useful. Although the German anti-poison act of 1887 prohibits the use of zinc as a coloring matter, it does not apply to its ordinary use in rubber compounding. They rule that zinc compounds not soluble in water may be used in rubber when and where the coloring matter is mixed in the mass before vulcanizing, or as a pigment on the surface if it is covered with a lacquer varnish. Specific gravity from 4.30 to 4.50.

CHARLTON WHITE.—See Lithopone.

CHINESE WHITE.—Another name for Zinc Oxide.

FARD'S SPANISH WHITE.—Also known as pearl white. A trinitrate of bismuth, and a white that, it is said, has a future in rubber compounding. It is not easily affected by atmospheric influences, or by the action of sulphurous compounds.

FULTON WHITE.—See Lithopone.

GRIFFITH'S WHITE is a sulphide of zinc of English manufacture, prepared by precipitation, and containing a certain proportion of magnesia.

KREMnitz WHITE was the name of a somewhat indefinite white. In some cases it was applied to white lead, but in others was given to bismuth white (oxide of bismuth) and often to white oxide of tin.

LITHOPONE (also LITHOPHONE).—A white pigment made by precipitating sulphate of zinc with barium sulphide. The barium sulphide is made from the native barytes by heating with charcoal, which reduces the sulphate to sulphide and polysulphide, which are soluble in water. The zinc sulphate is made by roasting zinc blende or the ore "black jack" under oxidizing conditions, which forms soluble sulphate of zinc. Both substances are dissolved in water, which frees them from many impurities, and the two solutions mixed, when zinc sulphide and barium sulphate both precipitate out as fine powder mixed with free sulphur from the polysulphide. The powder is dried and roasted, which drives off free sulphur and produces some free zinc oxide. Gives a fine white, but may turn gray on long exposure to light. This defect is not so bad for rubber as for painting. It is a constant white, and is largely used instead of oxide of zinc for white goods, particularly in the manufacture of druggists' and surgical sundries. The commercial article contains 70 per cent. of barium sulphate and 30 per cent. sulphide of zinc. Its specific gravity is 3.6 to 4.1.

MOUDAN WHITE OR MORAT WHITE.—This white came from the Pays de Vaud in Switzerland, Moudan and Morat being two towns in that district. It was a fine white clay with a silky luster and a fine grain. It resembles Spanish white and was often used in place of it.

OLEUM WHITE.—A high grade of sulphide of zinc, in which is a certain proportion of *blanc fixe*. It is a trifle heavier than a pure sulphide of zinc, but in practice has been found to be equal to if not better than either the sulphide or oxide of zinc in the manufacture of certain white rubbers. It is essentially lithopone.

ORR'S WHITE.—See Lithopone.

PONOLITH.—Another name for Lithopone.

ROSS'S WHITE.—See Lithopone.

ROUEN WHITE was a marly clay found near Rouen in France, prepared for use by levigation. In most respects it resembles Bougival white.

RUBBER MAKERS' WHITE.—Another name for Lithopone.

SPANISH WHITE is a name now often given to a good quality of whiting, but originally given to a good kaolin clay prepared for sale first by levigation, then by treatment with vinegar, which separated out any calcium carbonate it contained, then washing well and drying.

TROYE'S WHITE is a carbonate of lime, and, therefore, was in all respects like the modern whiting. It was a very common pigment at one time and much used for a variety of purposes. Specific gravity about 2.70.

ZINC CARBONATE.—This is a form of zinc rarely known today in rubber mills. The first white rubber, however, was made of it under a patent granted to the late Henry G. Tyer. It is a white powder, of the specific gravity of 4.45, and is made by mixing a solution of equal quantities of sulphate of zinc and carbonate of sodium, and subsequently the boiling of the white precipitate formed for a short time.

ZINC OXIDE is used more than any other coloring matter in the production of white rubber. It is especially valuable because during the process of vulcanization it increases the whiteness of the goods. This is because the part of the zinc oxide that is turned into the zinc sulphide is a stronger white than the first. Oxide of zinc made of pure spelter is the best. Where lead and zinc ores are found together it sometimes happens that

the oxide contains a certain amount of lead, as lead sulphate, and then its value as a coloring matter is injured.

Zinc oxide is prepared by two processes: French process, in which spelter or metallic zinc is the raw material, and American process, in which ores of zinc are the raw materials. French process oxides of American manufacture are known as "Florence zinc."

French process zinc oxide is sold in three grades, designated as "White Seal," "Green Seal" and "Red Seal."

White Seal is brilliantly white, of large volume and extreme fineness. It weighs 150 pounds to the barrel, as compared with 300 pounds of other oxides.

Green Seal is equal in brilliancy of color to White Seal, but is less voluminous.

Red Seal is the cheapest of the three grades and is neither so white nor so smooth in texture as the others.

American process zinc oxides for the rubber trade are of two brands, "Special" and "XX Red."

Special is particularly free from lead, containing less than 0.1 per cent. of protoxide. It is intended for use in compounding white rubber and can be used in any mixture without changing color. It is very smooth and free from mechanical impurities.

XX Red is an oxide for mechanical rubber goods, free from mechanical impurities. It contains up to 0.2 per cent. of protoxide of lead and is not so white as the "Special" brand. The specific gravity of zinc oxide is 5.61. It is sometimes known as Chinese white. A certain percentage of this oxide is often added to dark-colored goods to increase the resiliency of the rubber. It also increases the hardness of a compound where soft gums are used. Manufacturers in insulated wire find that it increases the insulating qualities of rubber when added in moderate quantity.

A very simple test for zinc oxide is as follows: Put a small quantity in a test tube or vial and add diluted muriatic acid (such as can be obtained in any drug store); agitate to dissolve all lumps, and if it be commercially pure oxide of zinc, no residue



will remain. The only adulterant likely to be found which would not leave a sediment would effervesce violently. Should the addition of acid to the pigment produce sulphureted hydrogen, the odor of which is unmistakable, no doubt would exist that the sample is not oxide of zinc and probably a much cheaper pigment. There are many pigments on the market called zinc and containing some zinc in various forms, which have their uses, but should not be confused with straight oxide of zinc.

**ZINC SULPHIDE.**—This is a white that is fully equal to the popular oxide, and does not alter its tint under the influence of sulphur and heat. It is said to exert a distinctly preservative action upon india rubber. Sulphide of zinc, pure and in combination with other materials, and under various names, has been sold very largely to rubber manufacturers. It is deemed especially valuable in white goods cured with dry heat. It is used in high grade white stocks, and in pink dental rubber. It also assists in the vulcanization of rubber. Zinc oxide may be replaced entirely or in part with zinc sulphide pigment. The manufacture of zinc sulphide whites is an intricate chemical process. They are chemically made by a double precipitation process, are furnaceed at a very high temperature, and carefully washed and dried, producing a white of exceptional strength and body. No white pigment made possesses greater uniformity than the standard makes of zinc sulphide whites. The specific gravity of zinc sulphide is 3.98.

**ZINC WHITE.**—This is another name for Zinc Oxide.

#### YELLOW.

**YELLOWS** are not often demanded in rubber work, except in a few fancy articles and labels. The most common is that produced by the golden sulphuret of antimony, but color is not what is sought in the use of that ingredient, but rather the excellent rubber produced by it when used instead of sulphur. Other mineral yellows used are strontium, chromium, cadmium, barium, and zinc compounds.

**ANTIMONY GOLDEN SULPHIDE.**—This is the pentasulphide much used for high-grade red rubber goods, although its coloring effect is mild and it is esteemed rather for its influence on

the texture and quality of vulcanized rubber. See under vulcanizing ingredients.

**ARSENIC YELLOW** (also known as King's yellow), is a term applied to sulphide of arsenic. A cheap grade of this, which is really only an imitation, is manufactured by mixing together litharge and white arsenic, and grinding the product. Either of these, of course, is poisonous, and they are very rarely used or needed in connection with rubber. The specific gravity of arsenic yellow is 3.48. Although a sulphide, there is not enough sulphur in its composition to vulcanize india rubber. On account of its poisonous properties, this yellow has been largely superseded commercially by the comparatively harmless chrome yellows. Another name for this color is orpiment. It was often used in rubber compounds of twenty years ago. A small quantity in white zinc stock takes off the glaring white effect, and produces a handsome cream white. It must be an impalpable powder to bring out the color.

**AUREOLIN**.—A very handsome color, and one that is stable and brilliant. It is a double nitrite of cobalt and potassium. The color stands the light well, and sulphur compounds have little influence upon it. This is chiefly used for surface work.

**BARBERRY YELLOW**.—Made from the root or bark of the *Barberis vulgaris*. It is largely used in coloring leather surfaces, and, in connection with gamboge, is said to be useful in rubber work.

**CADMIUM YELLOW**.—This is cadmium sulphide and is the best pigment for producing yellow in a rubber compound. It does not injure the elasticity or strength of the india rubber in any way, and, while it has no special effect on vulcanization, perhaps hurries it a little. It is not injurious to the health of persons using it, and is generally used for surface ornamentation of toys, etc. It is sometimes mixed with yellow sulphide of tin to cheapen it. While cadmium was ruled against in the German anti-poison act, the sulphides of this metal were made an exception and said to be safe. In dental plates, however, where the coloring matter was used in large quantities, it was advised against. The costliness of cadmium yellow bars its general use in rubber. Its specific gravity is 4.58.

CHROME YELLOW.—Ordinarily the chromate of lead, which is largely used as a pigment. It is somewhat poisonous and is apt to oxidize organic substances, particularly if sulphur be present. Has been used in the surface ornamentation of rubber toys, but such use is generally condemned. The only chrome yellows that are really valuable for rubber work are the chromate of zinc, or possibly the chromate of strontium.

COBALT YELLOW.—This is another name for aureolin.

DUTCH PINK is the name given to some common yellow lake pigments made from Persian berries, quercitron bark, fustic, etc., on a base of China clay or whiting. At one time a blue Dutch pink was known, prepared from the woad plant.

GAMBOGE YELLOW.—Obtained from the *Garicinia morella*. It contains from 20 to 25 per cent. of gum, 65 per cent. of resin, 3 per cent. of volatile oil. It is soluble particularly in spirits, in a number of oily liquids, and partially in water. Finely pulverized gamboge may be mixed with rubber, and is said to be a preservative of it.

YELLOW OCHER.—There are several ochers, all of them being practically oxides of iron mixed with clay. They are earthy substances of no particular reaction, very stable, having a specific gravity of about 5.00. Their low cost renders them available for almost any work, but the colors produced are not especially beautiful.

ZINC YELLOW.—This color is chromate of zinc and potassium. It is of light lemon color and permanent. It is not affected by sulphur and can be mixed with other pigments.

## CHAPTER XI.

### ACIDS, ALKALIES, AND THEIR DERIVATIVES USED IN RUBBER MANUFACTURE.

As a rule neither acids nor alkalies, in the strict sense of the term, are largely used in ordinary rubber compounding. In a great many of the processes, however, that go far to make up finished goods, acids are used, as, for example, in those employed in the reclaiming of rubber chemically. Alkalies also are most necessary, a notable example being the use of caustic potash and caustic soda solutions in removing sulphur from manufactured goods. A great variety of uses other than these may be indicated.

ACETIC ACID.—This is usually obtained by the dry distillation of wood, peat, or sawdust. The strongest form is known as glacial and occurs in large watery crystals, readily liquefied. The common commercial acid usually has a brown or yellowish color, due to impurity. The pure acid is colorless. Its specific gravity is 1.05, and it has the characteristic odor familiar in vinegar. As an acid it is not very corrosive, and its compounds are easily decomposed by mineral acids. It is quite volatile. The primary use of this acid in connection with india rubber is in the coagulation of rubber milk. It is a prominent component part of the smoke used in coagulating fine Para rubber. It has also been used in the Vaughn process for coagulating balata, and in the manufacture of certain substitutes like linoxin, parkesine, etc.; in connection with nitro-cellulose and castor oil in the production of certain waterproofing compositions; by Brooman in separating whiting, white lead oxides, etc., from vulcanized rubber; and in shoemakers' blackings in connection with caoutchouc oil, vinegar, molasses, and lampblack.

ALUM.—A general term for several chemical compounds of aluminum, potassium, chromium, and ammonium. Common alum is the double sulphate of potassium and aluminum, having a

specific gravity of 1.7 and containing 45 per cent. of water of crystallization, one-quarter of which is expelled on heating to 140 degrees F. It is soluble in water  $9\frac{1}{2}$  parts per 100 when cold, 357 parts per 100 when hot. Chrome alum is a double sulphate of chromium and potassium, its specific gravity being 2.7, and containing 43 per cent. water of crystallization, which is almost entirely lost at 392 degrees F. It occurs as dull purple crystals, slowly soluble in water to 20 per cent. in the cold and 50 per cent. in hot water. Its action on gelatine is remarkable for its hardening qualities. Ammonia alum, the double sulphate of aluminum and ammonia, is largely used in place of common alum. It contains 48 per cent. of water of crystallization and has a specific gravity of 1.63. Strongly heated, it yields sulphate of ammonia, water and a very small quantity of sulphuric acid, while alumina is left behind. It is soluble in water 13 per cent. cold, 422 per cent. hot. Roman alum has the same general characteristics as common alum, but contains a little more alumina.

Alum is used in many of the shower-proof mixtures for cloths of the cravenette order, that are today bought and made up by manufacturers of mackintoshes. It is also sometimes used in the manufacture of sponge rubber. By Garnier's process it is also used in spirituous solution to cure rubber without heat by mixing with it. Used also in Wray's substitute for gutta-percha. Alum was used in Payne's gutta-percha compounds for proofing, varnishing, and paints. Ghislin, who prepared some curious compounds from seaweed and india rubber, mixed alum, gelatine, and metallic oxides in his compounds. It is also sometimes used with sulphate of iron and soap, in a water mixture with boiled linseed oil, to make flexible water-proofing compounds.

ALUMINUM SULPHATE.—The active principle of alum. Often sold as concentrated alum. Occurs commercially as white square cakes, somewhat transparent, and capable of being cut with a knife. Readily soluble in water, and contains a small quantity of free sulphuric acid, potassa, and soda alum. Its specific gravity is about 4.00, water of crystallization 48 per cent. Its composition indicates a usefulness in compounding



sponge rubbers. Used in linseed oil compounds, for wagon covers. See Alum.

AMMONIA, at ordinary temperature, is a colorless gas of well-known odor and sharp, biting taste. It is usually met with in the arts in watery solution, the specific gravity of which varies with the amount of ammonia gas dissolved. The strongest, sometimes called caustic ammonia, contains 32.5 per cent. of the gas, and has a specific gravity of .875. Ordinary commercial ammonia contains 9.5 per cent. ammonia gas and its specific gravity is 0.96. The weakest usually has a percentage of 5.5 and a specific gravity of .978. Ammonia has a powerful solvent action upon sulphur, is alkaline in its nature, and very volatile, so that much care is requisite in handling it. It has long been known to have a preservative effect upon india rubber; for example, low grade African rubbers are often treated with ammonia to neutralize the smell, and also to toughen the rubber. In the cold-curing process a saucer of ammonia put in the bottom of the vapor room will effectually neutralize the fumes of chloride of sulphur. It is also advised to wash with an ammonia solution vulcanite that has begun to perish. Soft rubber goods also are preserved, according to Dr. Pol, by the immersion for an hour in a solution made of 1 part of ammonia, and 2 parts of water.

Sievier dissolved india rubber in ammonia, leaving it in a closed vessel for a long time, after which he heated the solution and absorbed the ammonia gas in cold water. Concentrated liquor of ammonia is added to milk of the rubber tree to preserve it for transportation. Where vegetable fibers are reduced to cellulose and mixed with india rubber, the rubber is first steeped in ammonia and then dissolved in some suitable solvent. Newton mixed ammonia with india rubber and gutta-percha, and then treated the gum with chlorine, making a white, hard compound, which he claimed would stand all varieties of climates, acids, greases, etc.

AMMONIUM CARBONATE, obtained during the dry distillation of coal in the manufacture of illuminating gas, is a white crystalline powder of very penetrating smell, from which quality it takes its popular name of smelling salts. Exposed to air, it

decomposes, evolving ammonia and becoming converted into bicarbonate. It is used industrially for the removal of grease from cloth and cleaning woolen fabrics. Carbonate of ammonia is used also in the manufacture of sponge rubber, and in hollow work, where its expansive force is utilized to mold the article effectually.

AMMONIUM CHLORIDE.—Also known as muriate of ammonia, or sal ammoniac. Obtained largely from gas works liquor. Specific gravity 1.5. Usually occurs in small crystals. When dissolving in water a considerable reduction of temperature occurs, and this has rendered it valuable for cooling purposes. At temperatures above 212 degrees F. it is completely evaporated, and a decomposition into ammonia and muriatic acid occurs. It is used in certain packings in which iron filings are incorporated.

AMMONIUM TUNGSTATE.—A crystalline body which is very soluble in water and becomes covered with a white bloom or efflorescence on exposure to the air. Used with boracic acid, kauri, borax, and rubber in the production of the woodite fire-proof composition.

ANILINE.—An oily liquid, colorless when pure but ordinarily straw color. Its specific gravity is 1.02 at 60 degrees F. and its boiling point 364.6 degrees F. Commercially, aniline is obtained by a series of chemical transformations, beginning with coal tar. Among the products liberated from coal tar by distillation is benzol. Benzol, when acted upon under suitable conditions with mixed nitric and sulphuric acids, is converted into nitrobenzol. Nitrobenzol may further be acted upon and chemically "reduced" to aniline oil by treatment with dilute hydrochloric acid in the presence of a slow feed of common cast iron borings, both acid and borings being in definite proportion to the charge of nitrobenzol to be reduced. If sold as pure aniline should not contain over one-half of one per cent. of water, and should be free of nitrobenzol. A delicate test for the presence of nitrobenzol in aniline oil is to shake a sample violently for a few minutes, and notice the color of the froth so produced. The merest trace of nitrobenzol present will give a very distinct yellow coloration.

In recent years the use of aniline in the manufacture of rubber goods has increased to large proportions. The chief function of aniline as a compounding ingredient is that it serves as a catalyzer, accelerating the combination of sulphur and rubber in the process of vulcanization. Its use is accompanied by a considerable degree of danger to the health of the workmen unless adequate measures are adopted to prevent its fumes being inhaled or the liquid coming in contact with the skin, through which it is readily absorbed.

An American process for reclaiming waste vulcanized rubber calls for its admixture with aniline oil and subsequent steam devulcanization.

Aniline was used by Parkes in the manufacture of parkesine. It is also a solvent for gutta-percha and in the laboratory is used in analytic work as a solvent for vulcanized rubber.

The so-called aniline dyes are derivatives of aniline.

ANTIMONY IODIDE.—A brownish-red crystalline mass, which yields a cinnabar-red powder. It is soluble in hot carbon bisulphide. Its specific gravity is 4.39. It was used by Parkes in vulcanizing india rubber.

BARIUM CHLORIDE.—A white crystalline powder. Its specific gravity is 3.05. To makers and users of sulphurets it affords a ready means of determining the presence of free sulphuric acid, so liable to occur in these bodies and so injurious to rubber compounds when present. A suspected sulphuret should be boiled for a moment with a little distilled water, the water filtered off, and a drop or two of a solution of barium chloride added; a white cloudiness that will settle in the form of a white powder proves the presence of sulphuric acid and such a sample should be rejected. Barium chloride is a powerful poison. Used with size and acid resin as a shower-proof mixture.

BLEACHING POWDER OR CHLORIDE OF LIME is a mixture of the chloride and hypochlorite of lime. Industrially, its chief use is for bleaching purposes, dependent upon the amount of chlorine it contains. Commercial bleaching powder is a white powder with a smell of peculiar character (chlorine) and gradually becoming moist on exposure to the air, while it gradually decomposes and absorbs water and carbonic acid. Even in closed

vessels decomposition occurs, and sometimes so suddenly and with such a rise of temperature that explosions occur. Hence it should always be used fresh and a guarantee obtained from the vendors (as is customary) of the quality of the article. Chloride of lime is the basis of a cold-curing process known as Caulbry's (which see). Gutta-percha boiled in it and then mixed with rosin and paraffin is used in insulation.

**BORACIC ACID.**—This is found native in the vapor which arises from certain volcanic rocks, in a saline incrustation in volcanic craters and in combination with borax. It appears in the form of pure white feathery crystals of the specific gravity of 1.43. Boracic acid is used with tungstate of ammonia, kauri, borax, and india rubber in the production of the woodite fire-proof compositions.

**BORAX.**—See Sodium Biborate.

**CALCIUM CHLORIDE.**—A crystalline substance containing about 50 per cent. of water of crystallization, which is lost on heating to 392 degrees F. The specific gravity is 1.61, and that of the dried form 2.21. Its extreme attraction for water makes it useful in obtaining a dry atmosphere in any closed receptacle. Its color is white. It absorbs ammonia readily and will give it up again on heating. It is used in bookbinders' cements.

**CALCIUM OXALATE.**—Quicklime slaked by water in which is oxalic acid is given this name. Used in certain gutta-percha compounds.

**CALCIUM OXIDE.**—See Quicklime.

**CALCIUM SULPHIDE.**—Lime that has been treated with hydrogen sulphide. It is an offensive smelling substance, of a dirty greenish-gray appearance, and is obtained in the process of purifying coal gas. Its specific gravity is about 2.20. It decomposes easily, giving off sulphureted hydrogen. It will absorb bisulphide of carbon and is soluble in alcohol. Its liability to oxidize should render it of questionable use in compounding. It was used by Hancock in vulcanizing india rubber.

**CARBOLIC ACID**, also known as phenol, is obtained chiefly during the destructive distillation of coal. Specific gravity 1.08.

The liquid is corrosive and is largely used for its antiseptic qualities. Carbohc acid is used as a preservative of rubber milk, where it is coagulated by the process some time employed by the Orinoco Co., in Venezuela. It has also been used in connection with a little ammonia to increase the elasticity of low-grade African gums, being used as a solution before the gums are washed. It is also used for treating fabrics, such as hose linings for fire and mill hose, to prevent deterioration and rotting. Used in certain fiber-made substitutes and in a rubber reclaiming process.

**CATECHU OR CUTCH.**—Known formerly as japan earth. Made from the sap of an East Indian tree, and used chiefly in dyeing. It is very astringent, and is soluble in water. It appears in commerce in dark-brown irregular lumps. Contains 40 to 50 per cent. of a peculiar tannic acid. Used in packings and goods made from the whaleite formulas. Johnson's artificial leather was made of catechu, rosin oil, linseed oil, turpentine, and starch, mixed with a little hot gutta-percha. A number of other compounds both with and without india rubber, contain catechu, but chiefly those which were compounded from gelatine, starch, and gluten. Catechu is mixed with gutta-percha in solution in order to make it harder.

**CHLORIDE OF LIME.**—See Bleaching Powder.

**CHROMIC ACID** is not readily obtained in a free state, but forms many well-known salts, such as chrome yellow (lead chromate), for instance. Chromic acid is analogous to sulphuric acid. Vulcanized rubber immersed in it at 140 degrees F. remained a month, and was apparently unharmed. It is also used in the manufacture of the substitute known as corkaline.

**CITRIC ACID.**—An organic acid that occurs in lemons, limes, and other citrous fruits. It is readily soluble in water. Has been used in the coagulation of balata. Vulcanized rubber immersed in it at 140 degrees F. remained a month, and was apparently unharmed.

**COPPER SULPHATE.**—Sometimes called blue or Cyprus vitriol. Occurs in commerce in masses of large blue crystals having a specific gravity of 2.28, and containing 36 per cent. of water of crystallization, and a varying additional percentage of



entangled moisture. Heated for some time at 212 degrees F., all the entangled water may be driven off, together with four-fifths of the water of crystallization, the residue being a bluish-white powder. Sulphate of copper solution is used in copper plating iron for secure attachment of rubber by vulcanization.

CREAM OF TARTAR.—See Potassium Acid Tartrate.

CUTCH.—See Catechu.

FORMIC ACID obtains its name from the fact that it was first obtained from the red ant. It is a fuming liquid with a pungent odor, boiling at 212 degrees F., specific gravity 1.22. It is now made from a mixture of starch, binoxide of manganese, sulphuric acid, and water. It has been suggested as an ideal precipitant for rubber milk. It is quite volatile, could be easily washed out, and would be found more beneficial to the rubber than many of the alkaline solutions now used.

HYDROCHLORIC ACID is known usually by its trade name of muriatic acid. It is one of the principal mineral acids and a common reagent in chemical analysis. Used in the arts in the form of a water solution, of which the strength varies from a specific gravity of 1.01 or 2 degrees Baumé with 2.02 per cent. acid to 1.21 or 26 degrees Baumé, with 42.85 per cent. acid. Each .01 increase of gravity corresponds to 1 degree Baumé and 2.02 per cent. of acid. It is corrosive to the skin and attacks nearly all metals. It has no action on caoutchouc and very little on oxidized linseed oil if the acid be dilute. With soda it forms common salt and with metals it forms chloride thereof. Hydrochloric acid, during the treatment of reclaimed rubber, turns whitening into calcium chloride. As the chloride is more soluble than sulphate of lime, much of it washes out during the vigorous cleansing that the rubber undergoes to remove the free acid. Hydrochloric acid, according to tests made by William Thompson, F.R.S., did not at all injure india rubber, although it was kept in it at a temperature of 140 degrees F. for a month. Concentrated hydrochloric acid has but little action on gutta-percha, and tubing made from it is therefore largely used in chemical factories for running this acid from one vessel to another. Hydrochloric acid is used in the manufacture of synthetic rubber from isoprene.

**HYDROGEN PEROXIDE.**—This is a powerful oxidizing agent, largely used as a bleaching agent, and also for neutralizing after chlorine bleaching. It comes in the form of a colorless liquid, and has a specific gravity of 1.45. Neither the alkaline nor the acid solutions of this reagent seems to impair vulcanized india rubber. In certain cases peroxide of hydrogen has been used in removing the bloom from rubber, which it does most effectively; besides, it seems to penetrate the surface of the rubber and dissolve the sulphur. It also has a curious effect on colors, brightening some reds wonderfully, dulling others, and rendering whites much whiter. One curious effect that it has upon india rubber is to bring out any surface imperfections to a marked degree.

**LEAD ACETATE OR SUGAR OF LEAD.**—This is used in certain rainproof compounds, one of which is 16 parts of compounded rubber, 128 parts of paraffin wax, 1 part of sugar of lead, 1 part of alum in powder. The india rubber compound used contains no sulphur. Used also in artificial rubber and artificial ivory. Specific gravity 2.50.

**LEAD NITRATE.**—A compound of lead and nitric acid containing 62.5 per cent. of lead. Its specific gravity is 4.58. It crackles when heated, detonates when thrown on red hot charcoal, and takes fire when ground with sulphur. Its color is white and it is largely used in dyeing and for making chrome yellow (which see). It is used with gums in the production of shower-proof mixtures with sugar of lead and alum.

**LIQUOR OF FLINT.**—See Sodium Silicate.

**MIMO-TANNIC ACID.**—See Catechu.

**MURIATE OF AMMONIA.**—See Ammonium Chloride.

**MURIATIC ACID.**—See Hydrochloric Acid.

**NITRIC ACID.**—A strongly acid liquid consisting of an aqueous solution of the pure acid. Its action is strongly oxidizing. Tin and powdered antimony are rapidly converted into their oxides, while turpentine, if poured into the strong acid, is attacked with almost explosive violence with the evolution of light and heat. Straw or sawdust may become ignited if impregnated with this acid. Cotton wool is converted by it into gun cotton. Rubber immersed in nitric acid at a temperature

of 140 degrees F., was injured in a few hours, and in a few days its elasticity was destroyed, while at the end of the month it was reduced to a pulp. Nitric acid attacks gutta-percha very powerfully, and evolves suffocating fumes of a deep red color, the gum meanwhile being reduced to a pasty mass which afterwards dries and becomes very brittle. According to H. L. Terry, nitric acid of any strength has a very deleterious effect upon india rubber, the action of the fuming acid being to form immediately an oxidized body of a resinous nature. He holds, therefore, that the weaker acid also injures the india rubber, although of course in a less degree. Nitric acid is used in the treatment of leather cuttings to reduce them to a glutinous mass before being mixed with india rubber, and is also used in making certain substitutes.

NUT-GALL.—An excrescence formed on the leaves of a species of oak called *Quercus infectonia*. It is used in the arts for the sake of the tannic acid it contains. There are three varieties in commerce—green, white and black. The black and the green are preferred. Those grown in warm countries are the best. Aleppo galls contain from 60 to 66 per cent. of tannic acid. There is a variety of nut-gall known as Chinese, imported from Japan, China, and Natal. The gall is somewhat bean-shaped or is covered with a yellow-gray felt. It contains from 60 to 70 per cent. of tannic acid. Nut-gall is used in certain places instead of tannin.

OIL OF VITRIOL.—See Sulphuric Acid.

OLEIC ACID.—An acid found in animal and vegetable oils, such as olive oil, sperm oil, etc. Specific gravity .890. It has been used in certain substitutes for hard rubber, like voltit, and by Hunt for recovering waste vulcanized rubber under heat, methylated spirit being added later to precipitate the rubber, which was then washed in a weak caustic soda.

OXALIC ACID occurs in transparent, colorless prisms, specific gravity 1.63, soluble in both cold and hot water. It is produced by either the action of potassium hydrate, or of nitric acid upon most organic compounds. It is very poisonous. Gutta-percha was cleansed by Lorimer's process by boiling in water mixed with this acid.

PHENOL.—See Carbolic Acid.

POTASSIUM ACID TARTRATE OR CREAM OF TARTAR.—A white crystalline substance with an acid taste, a very common ingredient in baking powders; also called potassium bitartrate. Specific gravity 1.96. It is made from purified tartar, or argol. It is used in artificial ivory made from resins in solution.

POTASSIUM ARSENATE.—A very soluble compound of arsenic with potash forming what is known as Fowler's solution. In the dry state it is a white powder soluble in alcohol up to 4 per cent. Potassium arsenate was used by Forster, in his earliest experiments, to vulcanize partially a compound made up of india rubber and shellac.

POTASSIUM BICHROMATE.—The principal compound of chromium, which occurs in the form of orange-red crystals, specific gravity 2.69. It is soluble in water and is largely used in dyeing. Mixed with sulphuric acid, it is used in bleaching palm oil and other fats. Bichromate of potassium is used in hardening the compound known as elastic glue; also used in Christia gums.

POTASSIUM BISULPHATE.—A white powder obtained as a by-product in chemical manufacturing. Soluble in twice its weight in cold water, and in half of its weight in boiling water. It contains sulphuric acid so loosely held in combination that it is driven off upon heating. Its specific gravity is 2.16.

POTASSIUM CARBONATE OR POTASH.—This substance is usually met with commercially in small, colorless crystals. It is prepared in a variety of ways and forms, and is the basis from which is derived what is called caustic potash. Pearl ash is a crude form of potash mixed with the caustic variety and a sulphuret of potassium. Used in certain proofing compounds where low heat is required for cure. It was used by Charles Hancock, mixed with water in a bath, to improve the quality of gutta-percha. He found, by boiling the gutta-percha in such a bath for an hour, that it did not oxidize in the open air as badly. An old-fashioned process for treating unvulcanized thread was to steep it in a hot solution of carbonate of potash, which greatly increased its strength. See Caustic Potash.

POTASSIUM CYANIDE.—A white crystalline substance, very

poisonous. Specific gravity 1.54. It is very easily decomposed, even on exposure to the air, absorbing carbonic acid and yielding prussic acid, which gives the salt its peculiar smell of peach kernels. The vapors thus given off are very poisonous. Cyanide of potassium was used by Brooman "to give clearness to the gum which was made from the ground vulcanized rubber, which had been treated with alkalies and acids to remove sulphur and adulterants."

POTASSIUM HYDROXIDE OR CAUSTIC POTASH.—As occurring in commerce, this is a white solid substance of the specific gravity of about 2.5. It is hard and brittle, and very destructive to animal and vegetable substances. It rapidly takes up water from the air, and may be used to obtain a dry atmosphere in a confined vessel. It is also a greedy absorbent of carbonic acid, becoming converted into the carbonate thereby. Solutions of potash should be clarified by allowing impurities to subside. Alcoholic caustic potash solution is used in analysis of vulcanized india rubber and was introduced by Henrichs, particularly to separate india rubber from india rubber substitute. Caustic potash is mixed with flowers of sulphur for boiling drawing rolls, the potash making the rubber more solid, while the sulphur gives a peculiar surface, making it better for drawing. Used in water solution to remove bloom from cured rubber. It is also used in certain substitutes for hard rubber like voltin. Caustic potash was early used in extracting the sulphur from ground vulcanized rubber.

POTASSIUM PERMANGANATE occurs in dark red prismatic crystals of greenish color which, when dissolved in water, give a purple red. It is a decided oxidizer, and is used as a disinfectant. It is also called chameleon mineral. Used in certain artificial leathers. Its specific gravity is 2.71.

QUICKLIME is the impure oxide of calcium obtained by burning chalk, marble, or limestone, or any carbonate of calcium. Its well-known attraction for water renders it unstable but also valuable where drying qualities are desired. Specific gravity about 3.30. Blizzard claimed to be able to make a perfectly transparent rubber by treating it with soda and water, in which was a little quicklime.



RECLAIMING SALT.—An alkaline composition made in Germany and used chiefly in the reclaiming of red and light-colored rubber waste.

RENNET is made from the inner lining of the true stomach of the sucking calf and gets its value from the gastric juice contained therein. The membrane, after treatment, is salted and stretched out to dry. It is advised in the Vaughn process for coagulating balata.

SAL AMMONIAC.—See Ammonium Chloride.

SALERATUS.—See Sodium Carbonate.

SALICYLIC ACID is obtained from the creeping plant known as wintergreen. It is prepared from the oil of wintergreen (oil of Gaultheria), which is distilled in large quantities in Luzerne county, Pennsylvania. It is also prepared synthetically; specific gravity 1.44. It is soluble in the following proportions: 1 part of the acid dissolves in 450 parts of water, or 2.4 of alcohol. It melts at 312 degrees to 314 degrees F. Salicylic acid was used in an artificial leather compound for reducing leather dust to a paste, after which it was mixed with glue under heat, and treated with an alkaline solution.

SAL SODA.—See Sodium Carbonate.

SALT.—See Sodium Chloride.

SALTPETER is niter or potassium nitrate. It is a white crystalline substance having a saline taste, specific gravity 2.08, and is a very strong oxidizer. It is used in the manufacture of artificial elaterite. In Gridley's process for recovering rubber, by exposing it to flame, saltpeter was added to remove the smell.

SILICON FLUORIDE is a colorless gas. What is used in the arts is a solution in water, forming a very acid fuming liquid. It is easily decomposed and may be used for etching glass if allowed to evaporate upon it under heat. It is prepared from flints or silica in some such form as sand or powdered glass. Used in treating meerschaum and paper pulp which, combined with certain resins, forms an artificial ivory.

SOAP.—Various kinds of soap are used in rubber manufacture. Pure Castile soap, for instance, is dissolved in rain water

and made into a soft soap that is used to "slick" molds that the rubber, during vulcanization, may not adhere to them. Some manufacturers use by preference white soda soap made from caustic soda and olive oil. Resin soaps are also used in certain shower-proof compounds. A further use for soap is in the manufacture of water varnishes for luster coats and blankets. A soap compound for wagon covers is made of 50 pounds of soap dissolved in 15 gallons of water, heated to 250 degrees F., to which is added 25 pounds of sulphide of zinc. A half pint of rubber dissolved in olive oil by heat is added to each gallon of the above mixture. Whiting, lampblack, or coloring matters may be added. Vulcanized rubber, beeswax, rosin oil, argillaceous earth, and alkaline soap form the basis of Sorel's substitute for rubber.

SOAP BARK.—Bark of a Venezuelan tree, *Pithecolobium bigeminum*. Its water extract is used to "slick" molds.

SODA.—See Sodium Carbonate.

SODIUM BIBORATE OR BORAX.—Sometimes also called tincal; a compound of soda and boracic acid. The purified commercial article contains about 4 per cent. of water of crystallization and is usually in the form of large odorless crystals, or a white powder obtained by grinding. The crystalline form has a specific gravity of 1.69. Borax is quite soluble in water, but not in alcohol or any of the common solvents for rubber. At a moderate heat borax loses water, and separates as a spongy mass called calcined borax, while at a higher heat it melts into borax glass. Immense deposits of it are found in western United States, and it is also found in India, Hungary, and other parts of the world. A good waterproof cement is made of a mixture of borax and shellac boiled in water. Borax, or a solution of biborate of sodium, has the property of dissolving many resins. Lascelles-Scott describes the manner in which an emulsion of rubber may be preserved by a borax solution. To a solution of rubber, in any one of the common solvents, a small portion of alcohol is added. This is mixed with a 2-5th saturated solution of borax, previously heated from 120 degrees to 140 degrees F. This is agitated until the temperature has cooled to the temperature of the air. From  $3\frac{1}{2}$  per cent. to  $4\frac{1}{2}$  per cent.

of india rubber should be present in the fluid when finished. A higher strength quickly separates and sometimes causes the entire quantity to coagulate. Madagascar or Sierra Leone rubbers are advised for borax solutions. Solutions of borated rubber are adapted for waterproofing and for preserving mats, marine bedding, etc. Borax is also advised for preserving rubber milk from coagulation. It is also an important ingredient in the water varnishes used for luster finish, for surface coats, army blankets, etc.; is used in waterproofing compounds composed of rubber, boracic acid, kauri, tungstate of ammonia; mixed with gutta-percha and shellac, it was used by Hancock as an insulating material.

**SODIUM BISULPHITE.**—Used for bleaching plantation rubber during coagulation.

**SODIUM CARBONATE.**—Also called sal soda, washing soda. Prepared from cryolite, salt, etc. Its specific gravity is 1.45, when crystallized. The crystalline form contains 64 per cent. of water of crystallization, of which one-half is driven off by gentle heating. It is found in the ashes of many plants, is produced artificially in large quantities from common salt, and is used as an alkaline agent in many chemical industries. India rubber, burnt umber, japan, and a coloring matter are mixed with a certain proportion of sal soda for a waterproofing composition. Under the common name *saleratus*, carbonate of soda is used as follows: Instead of sunning surface goods, like rubber coats and blankets, they are often brushed over with a mixture of *saleratus* and powdered charcoal immediately after the stock leaves the calender. Sometimes the *saleratus* is left out and only charcoal is used.

**SODIUM CHLORIDE** (or common salt) has a specific gravity of 2.3. It is a very stable compound, soluble in water at the ordinary temperature to the extent of 36 per cent., and at the boiling point, of 39 per cent. At the freezing point water will take up  $5\frac{1}{2}$  per cent. of common salt. It is used in coagulating many of the rubber latexes. Salt is viewed with considerable distrust by ordinary manipulators of rubber. Payne, however, treated gutta-percha scraps by boiling water, salt, and oil of vitriol, to get a solution to which he added other gums and metallic

oxides to get a waterproofing mixture. Cooley made artificial leather of gutta-percha dissolved in rosin oil, and added 25 per cent. or more salt, to which he added starch or other saccharine substances. Salt solution is used in washing the compound known as tremenol. It is also used in shower-proofing compounds, in connection with paraffin and sulphuric acid.

**SODIUM HYDROXIDE OR CAUSTIC SODA.**—Specific gravity 2.13. The chief use of this, in the manufacture of rubber goods, is in the dissolving of sulphur that is formed on the surface of goods, and which is known as bloom. According to H. L. Terry, F.I.C., the bulk of the alkali supplied to rubber manufacturers in England is used in removing the sulphur from elastic thread. It is also used in treating tobacco pouches, fine sheet articles, and blacks, reds, or maroons, that should have a good clear color. The boiling of rubber goods is usually done in wooden tanks in which steam can be passed, and sometimes in slate tanks, as iron is attacked by the alkali. On good grades of rubber, caustic soda has no action at all. Where a large quantity of resin is present, however, it may dissolve a part of it, forming resinate of soda. Heavily compounded rubbers, whether they contain substitutes, gums, or compounds, unless they are absolutely inert, are also liable to be attacked through the dissolution of their ingredients. Camille describes a process whereby shoddy is treated with a solution of carbonate of soda in devulcanization. In this, the rubber is boiled several hours in a solution of caustic soda, the result being that it will sheet when the process is completed. Rostaing purified gutta-percha by boiling in caustic soda, or in a mixture of caustic soda and potash in water.

The largest use for caustic soda in the rubber industry is found in the reclaiming of waste rubber by the alkali processes.

**SODIUM HYPOSULPHITE.**—A one per cent. solution is used for removing traces of chlorine where its presence is suspected in india rubber.

**SODIUM PHOSPHATE.**—A crystalline colorless substance containing 60 per cent. of water, which is given up on heating to 248 degrees F., leaving behind a dry mass. The commercial article frequently contains sulphate of soda as an impurity. The

crystals have a specific gravity of 1.5, melt at 95 degrees F., and are readily soluble in water. By long drying at 113 degrees F., the water of crystallization may be entirely driven off. The presence of this material is called for in a certain compound for dental vulcanite, where it is incorporated with rubber, sulphur, and phosphate of lime, the idea being that less sulphur is required for vulcanization than in the ordinary compounds.

SODIUM SILICATE.—See Soluble Glass.

SODIUM SULPHATE occurs commercially in colorless crystals which deteriorate in contact with the air, and hence should be kept in well-closed vessels. It contains a very large amount—nearly 60 per cent.—of water of crystallization, which is yielded on heating to 302 degrees F. Its reaction is alkaline. Sulphate of soda was used by Hancock in vulcanizing gutta-percha. Its specific gravity is 1.48.

SODIUM TUNGSTATE.—Prepared commercially from wolfram ore and soda ash; usually contains about 14 per cent. water of crystallization; and is in the form of colorless crystals. Mixed with a solvent such as methylated ether, it is added to soluble gun cotton, castor oil, and gum copal, forming a substitute for india rubber. Specific gravity 3.256.

SOLUBLE GLASS (known also as waterglass) is a silicate of soda or potash. It is usually sold in solutions of varying density, the commonest being 33 degrees and 66 degrees, by which is meant that the solution contains either one-third or two-thirds solid waterglass. Acids readily precipitate the silica from these solutions as a gelatinous mass. It is used in certain shower-proof compounds and in compounds of the algin type.

SULPHURIC ACID (called also oil of vitriol), when pure, is a colorless, heavy, oily liquid. It is very corrosive, and has a great attraction for water; hence wood and other organic bodies are charred in the heat evolved by it depriving them of their water. The specific gravity of the commercial acid is usually about 1.83, or 66 degrees Baumé, containing 94 per cent. of acid. Sulphuric acid is used in the coagulation of Madagascar rubber. The Orinoco Co., in Venezuela, are also said to have coagulated india rubber by mixing the milk of the *Hevea* with sulphuric and carbolic acid. Commercial sulphuric acid is said



to coagulate 55 times its volume of gum, while the carbolic acid acts as an antiseptic in the juice, improving its keeping qualities. It is a question whether rubber treated this way is as good as that obtained by the smoking process. Rubber immersed in sulphuric acid at 140 degrees F. remained a month and came out stronger, apparently, than when it went in. Sulphuric acid is used in paste blacking, mixed with bone black, vinegar, molasses, and caoutchouc oil. Concentrated sulphuric acid colors gutta-percha brown, throwing off at the same time sulphurous acid fumes. Nevertheless, a paste of this acid and charcoal was added by Hancock to gutta-percha to make it pliable. Sulphuric acid may be expected to attack vulcanized rubber compounds in which there are large proportions of chalk, lead, or zinc oxides. Sulphuric acid is very largely used in destroying the fiber found in ground waste rubber; indeed it is the basis of what is known as the acid reclaiming process. When thus used the acid turns whiting into sulphate of lime.

TANNIC ACID.—See Tannin.

TANNIN includes a number of substances, some of which are crystalline and others amorphous, having marked astringent properties and no smell. Tannins are acid, soluble in water and alcohol, and yield precipitates with most metallic oxides. Tannin is the active principle of oak bark, hemlock bark, catechu, and many other materials commonly used for tanning hides. Pure tannin is a light powder of a yellow-greenish hue, specific gravity 1.10. Its solution precipitates glue. It is used with sulphate of alumina, waterglass, and glue in shower-proofing. Tannin has been claimed to be injurious to rubber, the reason being that rubber thread used in gorings is often destroyed at points close to its junction with the leather. It is more likely, however, that it is the oil in the leather that effects the destruction. Tannin was largely employed by Austin G. Day in many of his "kerite" compounds with excellent effect. It is also used in the manufacture of certain puncture fluids, together with glue and glycerine.

TARTARIC ACID is found usually in the form of transparent colorless prisms, which have an agreeable acid taste, are not affected by the action of the atmosphere, and are soluble in either alcohol or water. Specific gravity 1.66 to 1.76. This acid is

very abundant in the vegetable kingdom, being found in many fruits. Used under Vaughn's patent in coagulating balata. Vulcanized rubber immersed in tartaric acid at 140 degrees F. remained a month, and was apparently unharmed.

TUNGSTIC ACID is derived chiefly from wolfram, which is a tungstate of iron and manganese. Tungstic acid is analogous to sulphuric and chromic acid. It has been used in connection with paraffin, gelatine, and metallic oxides in proofing compounds.

ZINC CHLORIDE was known formerly as butter of zinc. It is formed by burning zinc in chlorine gas, or by dissolving it in hydrochloric acid, the solution being evaporated. Its specific gravity is 2.75. The anhydrous form is a whitish-gray mass which readily fuses, and can be sublimed at a high temperature. It deliquesces on exposure to the air, and is readily soluble in water, acting in a concentrated state as a powerful caustic. One of the best processes ever known for reducing the fiber in recovering rubber was that in which this substance was employed instead of acid. A boiling solution of chloride of zinc was used in deodorizing by Brockedon, who also mixed it with gutta-percha, adding sulphur and vulcanizing the gum. Hancock also subjected gutta-percha for a moment or two to binoxide of nitrogen, then immersing it in a boiling solution of chloride of zinc, which he claimed greatly improved its quality.

ZINC IODIDE.—A very unstable substance. A white granular powder, odorless. Chiefly used in medicine. It was used by Hancock to assist in the vulcanization of india rubber. Specific gravity 4.70.

## CHAPTER XII.

### VEGETABLE, MINERAL, AND ANIMAL OILS USED IN RUBBER COMPOUNDS AND SOLUTIONS.

THE use of oils in rubber manufacture has kept pace fully with the use of gums, substitutes, and reclaimed rubber. The addition of earthy or metallic or vegetable ingredients in dry mixing has rendered many a good rubber somewhat intractable—a fault which the right oil has often rectified. As a rule, vegetable oils are chosen, as they are rarely harmful to the gum. Many mineral oils are also freely incorporated in certain compounds. Animal oils have always been viewed with more or less suspicion, however, and with good reason, for manufacturers have constantly before them rubber goods that have lost their life and elasticity through contact with lubricants made of such oils and fats. Nevertheless certain of them may be and are used. The essential or volatile oils are used to a certain extent in rubber manufacture. These oils, as a rule, give the peculiar odors of plants from which they are derived. Their use in rubber is to impart to it a pleasing odor.

ALUMINUM LANOLATE.—This is a product precipitated from French wool grease, made by adding a solution of alum. It is dissolved in mineral oil, forming a jelly-like mass which is said to compound readily with either india rubber or gutta-percha, and is soluble in any of their solvents. It is possible that this may have both softening and preservative influences on india rubber, as is claimed, but it should be used with considerable caution.

BLOWN OILS.—These are prepared by heating fixed vegetable oils in a jacketed kettle and blowing a current of air through the fluid. Under this treatment, oils become much more dense, viscous, or even solid by combining with oxygen. In many physical aspects they resemble castor oil, but differ in that they can be mixed with mineral oils and as a rule are not easily soluble

in alcohol. Blown oils made from linseed oil, rape oil, poppyseed oil, and cottonseed oil are sometimes used in the manufacture of rubber substitutes instead of the raw oils. Known also as thickened oils, base oils, soluble castor oil, etc.

**CAMPHOR OIL.**—A liquid of a light reddish-brown with a yellowish tint, and a strong camphor odor. Its specific gravity is 0.94. The Japanese oil varies in color from colorless through pale straw and yellow, to black, and has a specific gravity of 0.898 for the colorless to 0.99 for the very dark. This oil is used in the manufacture of celluloid varnishes, paints, lampblacks, etc. It is used also as an adulterant for such oils as sassafras oil. It is one of the best solvents for resins, and dissolves 46 per cent. of rosin, 9 per cent. copal, and 35 per cent. of mastic.

**CAOUTCHOUC OIL.**—Made by digesting 55 parts of india rubber in 450 parts of linseed oil. The principal large use for this oil is in Germany, particularly in the army, for coating various articles to prevent their rusting. The following substances are found in oil of caoutchouc: eupoine, butylene, caoutchoucine, isoprene, caoutchine, and heveene.

**CASTOR OIL.**—A colorless or pale greenish transparent oil, very viscous and thickening on exposure to the air. It has a higher specific gravity than any other known natural fatty oil—0.958. It is adulterated frequently with resin oil and rape, linseed, and cottonseed oils, especially the “blown” variety. Used in cheap proofings without rubber with kauri gum; also in collodion and rubber proofing. It is used in the production of substitutes like gum fibrine, and also with chloride of sulphur in producing amber-colored and white substitutes.

**CHOLESTERIN.**—See Lanichol.

**COD OIL OR COD-LIVER OIL** is obtained from the livers of codfish. Newfoundland and Norway are the principal manufacturing points. The finest is a very pale, clear, golden yellow, the color deepening to a brown in the second and third grades. Its specific gravity is 0.923 to 0.929. One part of oil is soluble in from 40 to 20 parts cold alcohol, or 30 to 17 parts hot alcohol. The lower grades are the more soluble. It is much adulterated. Is compounded with india rubber, beeswax, linseed oil, litharge,

and asphalt as a waterproofing for leather and with india rubber, beeswax, and turpentine as a dressing for hides.

COLZA OIL.—See Rapeseed Oil.

CONSOLIDATED OIL.—See Stearine.

CORN OIL OR MAIZE OIL.—Made from the seed of Indian corn, the plant known botanically as *Zea mays*. There are two processes of manufacture: (1) in which the seed germ is pressed before it is used for the manufacture of starch, which produces oil of a golden yellow color, and (2) where it is recovered from the residue of the fermentation vats where the corn has been used in the production of alcohol. This oil dissolves sparingly in alcohol, but very readily in acetone. The oil is almost without drying powers. Neither boiling nor the addition of lead when boiling gives it definite drying properties. If it is heated, however, and a current of air passed through it, and manganese borate mingled with it, it dries after a fashion. It is largely used at present in the manufacture of what are known as corn-oil substitutes. Specific gravity 0.921-0.928.

COTTONSEED OIL is expressed from the seeds of the cotton plant, usually the *Gossypium herbaceum*. The crude is of a ruby-red, almost black color. The refined is pale yellow and possesses a pleasant, nutty taste. The specific gravity is about 0.930. It is a semi-drying oil, and is rarely adulterated except when linseed oil is very cheap. On standing it deposits stearine in waxy flakes. It is much used in making substitutes for rubber. It is also used in the production of artificial elaterite, and with paraffin oil for canvas proofing. It is converted into "blown" oil.

CREOSOTE OIL is a distillate from wood tar. Specific gravity 1.04-1.09. It is an oily liquid with a smoky odor, and is antiseptic. It should be colorless but is usually yellow or brown, due to impurities or to exposure. The best is made from the beech. A similar oil is distilled from coal tar. It has been used as a preservative to coat the fabric of which cotton hose is made; with india rubber and sulphur it has also formed an insulating compound for telegraph wires.

EUCALIPTIA.—A fragrant, refreshing volatile oil. It is prepared from eucalyptus oil.



**EUCALYPTUS OIL.**—An aromatic oil found in the leaves of the *Eucalyptus globulus* in Australia. The odor of the oil is extremely pleasant, smelling not unlike oil of verbenia. Its specific gravity is about 0.900. It has great solvent power on all resins and gums, including india rubber and gutta-percha. With the addition of a little methylated spirit it will dissolve even kauri gum, cold. It is also used in dissolving asphalt for photograph varnish.

**FISH OIL.**—Obtained from all parts of the bodies of common fish by boiling. Fish whose livers yield oil commercially do not give fish oil, and those bodies that yield oil, do not give liver oils. Principally prepared from menhaden. Its specific gravity varies between .915 and .930. Fish oil is used in the manufacture of the substitute known as volenite. It is used, however, only as a vehicle for carrying resin into the fiber, being afterwards wholly removed.

**FRENCH WOOL GREASE.**—See Lanoline.

**GLYCERINE.**—A clear, viscous liquid without odor. When pure it has a specific gravity of 1.26. The glycerine of commerce is a by-product of soap manufacture. When fat (glycerine stearate) is heated with caustic alkali and water the alkali disengages and takes the place of the glycerine in the combination, forming soap or stearate of the alkali, which separates out as a solid, leaving the glycerine free in watery solution, from which it is recoverable. Glycerine is not acted upon by oxygen, and therefore more closely resembles mineral oils (such as are used in rubber mixing) than it does the drying oils that go to make up substitutes. It has absolutely no solvent action on rubber.

A recent German patent calls for the addition of glycerine because of its oil-resisting qualities. In the compound used are 6 pounds of rubber, and 1 pound of glycerine, together with whiting, litharge, and sulphur. A solution of glycerine and alkaline fluid is also used as a cleaning and polishing medium in the last stages of the manufacture of certain cut-sheet goods. Glycerine, combined with gelatine and borax, has been used as a wash for both black and red rubber surfaces.

Glycerine was the basis of a well-known deodorizing composition for india rubber, the other ingredients being of an alka-

line nature. A bath of glycerine has also been used for experimental work in vulcanizing india rubber, and also for rubber stamp making. In this kind of work, the mold and its contents are immersed in the glycerine so that the liquid just covers the top of the mold; heat is then applied to the glycerine, and the mold in turn becomes hot and the rubber vulcanizes. It is also used to a certain extent in good grades of white rubber, as it gives a softened effect to the compound. Glycerine, in connection with glue, gelatine, molasses, and tannin, is used in the manufacture of puncture fluids for tires. It is also used in clothing compounds, and in cellulose products, like pegamoid. Used in rubber, a little of it increases the resiliency of the product.

**HYDROLENE.**—A rubber assistant used in connection with the reclaiming of rubber, and also rubber compounding. It would seem to be a petroleum product, and in rubber reclaiming is used instead of stock oil or residuum.

**KEROSENE.**—An illuminating oil of the paraffin series of hydrocarbons. Its specific gravity varies from 0.78 to 0.81. It has a flashing point (open cup test) from 90 to 110 degrees F., and includes all the intermediate distillates from crude petroleum of specific gravity 0.76 to 0.83. Its color should be water white. In rubber work it is useful to impart and retain softness in stocks in which it is desirable to retain resiliency, as in certain solid playing balls. Also it is very freely used in the manipulation of high-grade compositions used in hard rubber manufacture. Calender rolls, mill rolls and zinc surfaces are kept coated with a film of kerosene to give the hard rubber composition a perfect surface, exclude air and lubricate the molds and dies. Its use for the purpose of effectually suppressing the loss and nuisance occasioned by floating lampblack in rubber mixing, has been patented recently. The color is agglomerated by damping and mixing with kerosene before addition to the general batch.

**JAPAN WAX.**—A white or pale-yellow vegetable fat, with a specific gravity of 0.97 to 0.98. It is used in wax matches, candles, and for adulterating beeswax. A special use for it, that has arisen within the last few years, is in the manufacture of cravenette cloths. Most of this vegetable wax is derived from the fruit kernels of a tree peculiar to Japan, which begins to

fruit at about 15 years, and sometimes bears heavily when it is over 100 years old. It reaches a height of 20 to 25 feet, and produces from 30 to 150 pounds of nuts annually. The best wax is made from nuts that have been kept over the winter, and generally speaking, the quality of the product improves with the age of the nut. The wax is extracted by crushing and steaming the nuts, and then subjecting the mass to pressure. A second wax is secured by re-pressing. One workman can handle about 150 pounds of raw mass in a day, and this produces about 16 pounds of wax.

The crude wax is cast into round molds of a little more than a pound each. It is next refined, the process used being a traditional one and peculiar to Japan. It is mixed with wood or charcoal, ash and water, thoroughly boiled, and dropped into cold water, so as to form what are called wax flowers. These are taken out and exposed to the sun for about 20 days, when the process of boiling, making the flowers, and sunning is repeated. The wax is then boiled a third time, and the best quality taken off the top while it is in a molten condition. Recently improved methods have begun to come into use, and the crude wax is treated with an alkaline solution.

*LALLEMANTIA* OIL is obtained from the seeds of the *Lallemantia iberica*, a plant cultivated in Russia. This is one of the best drying oils, being said to surpass even linseed oil, but its chief use is for illuminating purposes. In Europe it is said to have been used instead of linseed oil in rubber substitutes.

*LANICHOL*.—A product of lanolin (which see), made from the oil of sheep's wool. It combines with gutta-percha and india rubber in any proportion to a perfectly homogeneous mass. This grease does not oxidize and is wholly antiseptic. It has no smell, and is impervious to the action of alkalis or to dilute sulphuric acid. It is said that, used in connection with gutta-percha, the melting point is considerably raised, while it does not diminish the insulating property. An insulating compound given is 50 parts by weight of gutta-percha, 30 parts of india rubber, 20 parts lanichol. The inventor claims that it renders gutta-percha less liable to oxidation, improves its elasticity and tenacity, and

diminishes its liability to become sticky. Patented in the United States and Great Britain by Robert Hutchinson.

LANOLIN is also known as wool grease, recovered grease, and brown grease. It is the natural grease found in sheep's wool and recovered from it while the raw wool is being prepared for spinning. A similar grease, made from scoured woven goods, is known as Yorkshire grease. It is a thick yellow or brown offensive-smelling greasy paste. Commercial lanolin is lighter colored and consists of about 80 per cent. of pure wool fat and 20 per cent. of water. It possesses in a remarkable degree the property of taking up water without losing its vaseline-like consistency.

Lanolin, mixed with india rubber, works up into an exceedingly sticky mass, and is used as a medicinal plaster. It is said that, while it possesses the adhesive properties of the regular plaster, lanolin takes up the medicament, and while very sticky can be readily removed from the skin. It is used for the purpose of softening india rubber, and was advised for use in tires, as it was said to soften the compound, and to keep the tire from decay, and from consequent surface cracking. It was also said to be used in boot and shoe work.

LARD OIL is prepared by the cold pressing of lard, which is the fat of the hog. It is a colorless, limpid liquid, although poorer grades are brown. Its specific gravity is 0.915. It is frequently adulterated with rapeseed oil and cottonseed oil. Lard oil, mixed with powdered pumice stone into a thick paste, is used for polishing hard rubber.

LAVENDER OIL has no perfume when new, but develops it on being exposed to the air. It is distilled from the flowers of the *Lavandula vera*, and is used sometimes to deodorize rubber goods. Specific gravity 0.875-0.910.

LEMON OIL is obtained from fresh lemon peel. A very volatile yellow or colorless oil; specific gravity 0.858; soluble in bisulphide of carbon, and absolute alcohol; often adulterated with fixed oils and alcohol; dissolves sulphur, phosphorus, resin, and fats; used to deodorize certain proofing compounds. Cologne sometimes takes its place.

LINSEED OIL is pressed from the seeds of the flax plant (*Linum usitatissimum*), grown chiefly in India, Russia, and Argentina. The trade recognizes two qualities of Russian seed—yielding the Black Sea linseed oil, and the Baltic linseed oil—while that coming from India is known as East India oil. Of these, the Baltic is the best, and the East Indian the poorest in quality. The two lower grades are not up in quality, for the reason that the Black Sea seed contains a certain amount of hemp seed, while that from India is usually mixed with rape, cameline, and mustard seeds. The oil which is expressed from these seeds is of a golden yellow color, with a peculiar taste and odor. Specific gravity 0.935. Linseed oil becomes easily rancid in the open air, but when spread in thin films dries into an insoluble substance which has been called linoxyn. Linseed oil is adulterated sometimes by fish or mineral oils, and by resin oils. Old tanked linseed oil is used in the preparation of what is known as boiled oil; that is, it is concentrated by heat at a high temperature that it may more rapidly dry when used in varnish. This drying process is hastened by the addition of manganese dioxide, litharge, etc. Boiled linseed oil is much darker than raw oil, having a brown-red shade. It is also much more viscous and has a higher specific gravity. Boiled oil is adulterated in the same manner as is raw linseed oil, the adulterants being resin oils, resin, and mineral oils.

In rubber compounding linseed oil is very often used. A very simple formula for waterproofing canvas is india rubber, litharge, sulphur, and linseed oil. It is also used in rubber varnishes, to a certain extent in molded goods, and quite largely in hard rubber compounding. It is the basis of a great many of the sulphurized or vulcanized oil substitutes. Linseed oil that is intended for mixing in linoleum is exposed to the air until it is thoroughly oxidized. In this state it is insoluble in alcohol, chloroform, ether, and ordinary solvents.

LITHOGRAPHIC VARNISH is obtained by boiling linseed oil at a temperature higher than that at which boiled oil is prepared, nor are dryers added during the boiling. It is a perfectly clear, transparent substance, the best quality being nearly as light as raw linseed oil. There are two ordinary grades of lithographic



varnish. One is known as "burnt oil," which is obtained by bringing raw linseed oil up to its flash point, and allowing it to burn until the required thickness is reached, it being constantly stirred meanwhile. "Oxygenated oil" is a linseed oil varnish made by treating the oil with oxygen in jacketed kettles, heated by steam. The product is as light colored as raw linseed oil, but heavier. It is also more readily soluble in alcohol, and has marked drying powers.

MANGANATED LINSEED OIL is used in certain rubber compounds where more of a drying effect is needed than is found in the raw linseed oil. It is linseed oil that has been boiled with peroxide of manganese to increase its drying qualities. See Boiled Oil.

MIRBANE OIL.—See Nitrobenzene.

MUSTARD OIL.—Black mustard oil is obtained from the seeds of the *Sinapis nigra*. It possesses a mild taste, is of a brownish-yellow color, and in its chemical composition closely resembles rapeseed oil. It is a by-product and is largely used in soap making. Its specific gravity varies from 0.914 to 0.921. White mustard oil is made from the seeds of the *Sinapis alba*. It is yellow in color, and almost identical with black mustard oil. Used in making rubber substitutes.

NEATSFOOT OIL.—A pale-yellow or colorless oil, obtained from the feet of oxen by boiling in water. It has a smooth, pleasant taste. On standing it deposits stearine. It is largely adulterated with cheaper animal or vegetable and even mineral oils. Neatsfoot oil, mixed with gutta-percha, tallow, sweet oil, and oil of thyme, is used as a rust preventive. It is used in connection with beeswax, india rubber, and Burgundy pitch in a composition for dressing leathers or hides. Its specific gravity is 0.915 to 0.918.

NITROBENZENE OR NITROBENZOL (also called oil of mirbane and "imitation oil of bitter almonds") is a yellow aromatic, oily liquid of specific gravity 1.20, produced by the action of nitric acid on benzene. It is used in perfumery and turned out in great quantities for the manufacture of anilines. It is used also in certain insulating compounds in connection with asbestos,

powdered glass, vulcanized rubber, castor oil, resin oil, and celluloid in solution.

**OLEARGUM.**—A black viscid liquid leather dressing of an oily nature used as a dull finish wash for rubber boots. Its composition is a trade secret.

**OLIVE OIL** is expressed from the fruit of the olive tree, principally in the countries of Europe bordering on the Mediterranean. Its specific gravity is 0.916. It is adulterated frequently with cottonseed oil. Olive oil is used in taking impressions from type faces in the matrix in which rubber type is cured. Mayall suggested the mixing of olive oil with clay until it formed a soft putty, and then incorporating it with india rubber, the proportion being  $\frac{1}{4}$  pound of oil to 30 pounds of gum. The use of the oil enabled the goods to be more largely adulterated; he also used olive oil in connection with devulcanized rubber, not as a solvent, but because he claimed that it combined with the gum and improved its quality. Olive oil is also used in hard rubber compounding. Rubber is sometimes heated up in olive oil mixed with zinc, soap, and borax for a proofing solution. It is also used in the manufacture of pegamoid.

**ORRIS OIL** is prepared from orris root. It has the consistency of butter, melts at 100 degrees F., and is miscible with alcohol. Its odor is like that of violets. Is used in rubber as a deodorizer. Specific gravity 0.949.

**PALM OIL** is obtained from the fruit of various species of palm, principally from the west coast of Africa, and is known in commerce under as many names as there are ports of shipment. It is expressed in a very rough fashion by the natives, who stir the palm kernels in holes in the ground until fermentation sets in and the oil rises to the surface. They also sometimes press the oil from the fresh fruits. The harder grades of palm oil are yielded by the former process, the latter giving the finer oils. Palm oil varies in consistency. Its specific gravity is 0.945; its color yellow to reddish; its odor that of violets. It yields a soap readily with alkalis and dissolves in ether and in alcohol of 0.848 specific gravity. Palm oil is very rarely adulterated, unless it is done by the native gatherers, who sometimes add sand as a make-

weight. Commercially, where sand and water together exceed 2 per cent., an allowance is claimed from the seller.

White palm oil is that which has been bleached by heat, chemicals or exposure to the air. "Lagos oil" has about the same consistency as butter, while "Congo oil" is as thick as tallow. Palm oil is used largely in the manufacture of mechanical and dry-heat goods, chiefly to enable dry ingredients to mix more easily with india rubber. It has also been used in the recovery of waste rubber by mixing it with the finely ground rubber and exposing the mass to a heat of 572 degrees F. Palm oil residuum is used in connection with resin oil as an insulator. Palm oil is also used in the production of artificial elaterite.

PARAFFIN WAX is a petroleum product. It varies in specific gravity from 0.87 to 0.91 and in melting point from 118 to 135 degrees F. It is a waxy substance of a white color, much resembling spermaceti. It is not acted upon by most of the chemical reagents. It has many applications in the arts. In rubber work it serves somewhat as a lubricant to obtain a very smooth surface on rubber forced through dies in tubed work. Also in weather-proofing insulated wires and mixed with cottonseed oil it is used in certain canvas proofing.

PEPPERMINT OIL.—A greenish-yellow colorless oil becoming reddish with age; of strong aromatic odor, and warm, camphor-like, very pungent taste; specific gravity from 0.902 to 0.920; used in fine goods for its odor.

PETROLATUM or crude vaseline is a rubber-compounding ingredient very generally used, especially in mechanical goods. It is one of the numerous products of petroleum or rock oil, derived by distillation. These products are classed as follows: Light oils, including gasoline and naphtha; illuminating oils, kerosene; residuum or tar. From the latter subdivision is separable, by further increase of heat, heavy lubricating and paraffin oils, among which are petrolatum or vaseline and coke as a waste product.

It is separated from the residuum of crude petroleum which has been subjected to the vacuum process of distillation in contradistinction to the "cracking" process by which some of the natural constituents are chemically broken up to form new

bodies. The residuum being kept fluid by steam, the finely divided coke resulting from the distillation, is allowed to settle out and the clear oil drawn off and filtered through fuller's earth contained in cylinders, in order to remove the color and odors contained in it. Sometimes the oil recovered from the residuum is treated with sulphuric acid and potassium bichromate for the removal of certain impurities before the filtration. This is said to be the German process.

Petrolatum gains much of its value from its indifference to all chemical treatment. It is generally familiar as a dense product, dark greenish, translucent, slightly fluorescent, semi-solid, melting at about 100 degrees F., and having a specific gravity of 0.850. Its chemically inert quality peculiarly adapts petrolatum to use in rubber compounding where a non-oxidizing lubricant and softener is needed to facilitate manipulation of harsh or dry compounds, and not subsequently develop in the finished goods injurious or other undesirable qualities. Any oil will soften rubber, but for all around adaptability petrolatum excels all others.

Ordinarily 2 or 2½ per cent. of petrolatum is sufficient in any compound where its presence is needed, although 5 or even 7 per cent. may be employed in special cases. Cheap goods containing petrolatum will withstand drying out or hardening with age, a similar effect being produced by the use of soft coal tar. As regards the item of economy, petrolatum commends itself to the rubber manufacturer when considering the use of an oil ingredient in compounding. For all ordinary purposes, everything except perhaps the whitest goods, the dark filtered stock is entirely suitable and the price will be less than the light filtered stock.

PETROLEUM JELLY.—See Vaseline.

PETROLEUM OIL (also known as Rock Oil) is a dark, ill-smelling liquid, obtained from wells sunk in oil-bearing sands. Some Russian oils, however, are colorless. White Rangoon oil contains so much paraffin as to have the consistency of butter. The specific gravity of American petroleum varies from 0.8 to 0.85 or 0.9.

POPPYSEED OIL is obtained by pressing the seeds of the common poppy (*Papaver somniferum*). Commercially there are two grades, white and red. This oil has no odor; it is rarely adulterated with other oils, although occasionally sesame oil is found in it; it is an excellent drying oil, and its lower grades are used in the manufacture of soaps; its use in the rubber industry is chiefly in the manufacture of substitutes. Its specific gravity varies from 0.913 to 0.924.

RAPESEED OIL OR COLZA OIL is pale yellow in color, with an unpleasant, hard taste. Its specific gravity is about 0.916. It is largely adulterated with vegetable, mineral, or fish oils. It is obtained from the seeds of the *Brassica campestris*, and of several varieties of this genus which are cultivated. American oils from all of these are termed colza or rape oil indiscriminately. In Europe, however, rape is one kind of oil and colza is another. There are also what are called the summer oil and the winter oil, a distinction which is of no interest to rubber manufacturers. Rape oil is about half way between a semi-drying oil and a non-drying oil. It is used in the manufacture of rubber substitutes. Mixed with india rubber it has been used as a somewhat costly mixture for lubricating machinery.

ROSEMARY OIL.—An essential oil of the specific gravity 0.896. Colorless and having the odor of rosemary. Used with india rubber, paraffin, and spermaceti in waterproofing compounds, and, where rubber is present, to neutralize its odor.

ROSIN OIL.—Made by subjecting rosin to destructive distillation. Specific gravity 0.96-1.10. The resultant oil is heavier than mineral oils, and its chemical composition is quite involved. It is largely made up of hydrocarbons, with a certain amount of resin acids. Used in making a waterproof solution, by the addition of Japan wax and gum thus, in the manufacture of a solution for treating hides and leather. Used also in compounds for calking ships in which india rubber has a part, and is an important ingredient in the manufacture of guttaline. See Rosin.

RUSSIAN MINERAL OIL.—Petroleum from the Baku oil wells.

SHALE OIL.—Chiefly produced in Scotland from a dark, coal-like shale. It is similar in nearly all respects to petroleum oil. Used with asphaltum in certain insulating compounds.



**STEARINE.**—An important ingredient in animal and vegetable fats. It is quite solid, and increases the hardness and raises the melting point of fat. Commercially, stearine is also known as stearic acid and consolidated oil. It is an important element in the manufacture of cravenettes, where it is used with ozocerite, beeswax, paraffin, and Japan wax. Specific gravity 0.987.

**TALLOW.**—Beef tallow, when fresh, is almost white, free from disagreeable odor, and almost tasteless. On the other hand, foreign tallow runs from white to yellow and is often quite rancid. Tallow is often adulterated with rosin oil, coconut oil, cottonseed oil, and paraffin wax. It is used in non-drying cements in connection with slaked lime and india rubber. In connection with india rubber it is also used in the production of what was known as Derry's waterproof harness oil, which was made of india rubber, tallow, seal oil, and ivory black. An etching varnish is made of gutta-percha, turpentine, beeswax and tallow. A small amount of this was used by Hancock in compounding for softening gutta-percha. It is used with gutta-percha in shoemakers' wax, and also in certain proofing compounds with india rubber, pitch and linseed oil. A mixture of india rubber, beeswax, linseed oil and tallow makes an excellent dressing for leather.

**TAR OIL.**—An oil distilled from tar. It is a mixture of several lighter oils, and is made up of liquid hydrocarbons which hold in solution small quantities of anthracene, naphthalene and paraffin. It has been recommended as a coating for rubber, it being claimed that it has a preservative effect. It is also used in compounds for surface clothing.

**THYME OIL** (also called *origanum oil*) is extracted from the flowers and leaves of the *Thymus vulgaris*. It is yellowish-red in color; its specific gravity is 0.92; and it has a pungent taste. It is used to disguise the odor of ale cements.

**TURPENTINE.**—See Spirits of Turpentine.

**VASELINE** is the purified residue from the distillation of petroleum. Its specific gravity is .875 to .945. It is insoluble in water, barely soluble in cold, but soluble in boiling absolute alcohol, and in ether, bisulphide of carbon, oil of turpentine, benzene,

and benzol. It is the basis of a cheap waterproofing process, the other ingredients being silicate of soda, alum and hot water. Vaseline is used quite often in general compounding for its softening effects. It is also combined with menthol and gum olibanum in the manufacture of porous plasters. Vaseline has been used in the manufacture of substitutes similar to Rubberite. See Petrolatum.

VULCANIZED OIL.—These are solid dry sulphurized vegetable oils, commonly known as rubber substitutes.

WALNUT OIL.—Cold drawn oil is very fluid, almost colorless, and of an agreeable nutty flavor. Its specific gravity is 0.926. Hot pressed oil has a greenish tint and an acrid taste and smell. Is used in rubber substitutes, particularly in those in which peroxide of lead appears as a dryer.

WHITE DRYING OIL.—Bleached linseed oil.

WORMWOOD OIL.—A pungent essential oil distilled from the *Artemisia absinthium*; employed at an early day to deodorize spirits of turpentine when used in rubber.

## CHAPTER XIII.

### SOLVENTS USED IN COMMERCIAL AND PROOFING CEMENTS.

THE beginnings of the manufacture of india rubber consisted in operations with the gum in solution and it was a considerable time before the discovery of the present processes of dry mixing, which are employed in the production of the greater part of the rubber goods now made. There are certain lines, however, where the use of solvents is still both necessary and economical. In the mackintosh manufacture, for example, the rubber is in almost every instance spread in the form of solution, as a thinner coat can be spread in this way, offsetting the cost of the solvent. Many sheetings in various colors that only a few years ago were calendered, are now coated by the means of solution. In the making up of almost all lines of rubber goods, cements are necessary, and these are ordinarily made in the factory that produces the goods. The cements that are sold in bulk, such as channeling cements, for leather shoe manufacturing, as well as cements that are sold in smaller packages to repair men in the cycle industry, all consist of rubber and analogous gum treated with some suitable solvent. Rubber being a hydrocarbon is soluble in the usual hydrocarbon solvents. These are usually those not soluble in water and of an oily nature.

The following tables show the solubility of rubber. The first, which is taken from the "Journal of the Society of Chemical Industry," is a table of the solubility of masticated caoutchouc.

	Ceara Rubber	Para Negroheads	Sierra Leone Rubber
100 Parts of:			
Ethyl ether .....	2.6	3.6	4.6
Turpentine .....	4.5	5.0	4.6
Chloroform .....	3.0	3.7	3.0
Benzine .....	4.4	5.0	{ 4.0 4.7
Carbon bisulphide .....	0.4	None.	None.

Hoffer gives, as a result of his individual experiments, the following table of solubilities of well-dried india rubber:

Solvents	Percentage Dry Rubber
Bisulphide of carbon .....	65 to 70
Benzol .....	48 to 52
Oil of turpentine .....	50 to 52
Caoutchine .....	53 to 55
Ether .....	60 to 68
Camphene .....	53 to 58

The great differences in solubility between various grades of rubber have been found to be due largely to the amounts of resins that are contained in them. As these resins are soluble, and in some cases can be removed, it is important that rubber manufacturers not only appreciate their presence, but, where it is practicable, dissolve them out. These resins consist of abietic acid or similar body, according to Lascelles-Scott, who has tabulated their solubilities as follows:

## SOLUBILITY OF RUBBER RESINS.

Description of Rubber	Normal Resin (soluble in 85 p. c. Alcohol)	Description of Rubber	Normal Resin (soluble in 85 p. c. Alcohol)
Para .....	.91	Ceara .....	1.16
Para .....	.60	Assam .....	6.45
Para .....	1.62	Assam .....	4.88
Para .....	1.14	Burma .....	5.20
Para .....	.85	Rio .....	3.37
Madagascar .....	4.06	Africa (various) .....	8.23
Madagascar .....	5.22	Africa (various) .....	10.60
Madagascar .....	2.84	Africa (various) .....	6.71
Colombia .....	3.40	Mangabeira .....	8.43
Colombia .....	2.11	Origin unknown .....	11.14
Ceara .....	2.33	Origin unknown .....	7.27
Ceara .....	1.80	Origin unknown .....	16.56

In some of them oxygen is a component part, and they are all soluble in alcohol of 85 per cent. strength and upwards. It will be noticed from this table that Para rubber has the least percentage of resin, and, of course, is the most valuable. The samples containing the largest proportions of resin were unmistakably adulterated with other gums during collection.

C. O. Weber gives the percentage of resin in a number of samples of rubber as follows:

Grade of Rubber	Per Cent. Resin	Grade of Rubber	Per Cent. Resin
Para (fine) .....	1.3	Sierra Leone .....	9.7
Ceara .....	2.1	Assam .....	11.3
Colombian .....	3.8	Mangabeira .....	13.1
Mozambique .....	3.2	African ball No. 1.....	22.8
Rio Janeiro .....	5.2	African ball No. 2.....	26.1
Madagascar .....	8.2	African flake .....	63.9

Clayton Beadle and Henry P. Stevens in their investigation on the insoluble constituents of Ceara and Rambong rubbers found that the "insoluble" and "soluble" constituents are separated by allowing the rubber to swell in a large excess of benzene, when on long standing the heavier insoluble portion collects in the lower half of the solution, the rubber being recovered from the upper and lower halves, respectively, by spontaneous evaporation. The authors concluded that their analysis and physical tests showed that the insoluble matter plays the part of a sulphur carrier and vulcanizing agent, independent of the proportion of the nitrogenous substance it contains.

The patent of Frankenberg (English) covering the production of non-inflammable solutions of rubber is of exceeding interest as suggesting the use of new and safe solvents. Today few chlorohydrins are used, because of their expense, but a number of them are on the market and the cost is steadily being reduced. Frankenberg's solutions are produced by mixing rubber with carbon tetrachloride, dichlor-methane, trichlor-ethane, tetrachlor-ethane, or trichlor-benzol, alone or together. The rubber may be softened with coal-tar naphtha or other solvent before the above solvents are added.

#### RUBBER SOLVENTS.

ACETONE is a colorless mobile liquid, with a very unpleasant taste and peculiar odor, and outwardly resembling alcohol. Specific gravity 0.797. It is a good solvent for many organic substances, and for many gums and resins. Acetone is produced by the destructive distillation of acetate of lime, which is one of the chemicals made from the products of wood distillation. It has a specific gravity of 0.80, boiling point of 134 degrees F. It is a solvent for rubber resins, dissolving about 18 per cent. of Pontianak resin while hot and is recommended as a solvent for use in analysis of rubber, as it is without action on the gum.

ALCOHOL, when pure, is a colorless, thin, mobile liquid, of a somewhat disagreeable smell, and specific gravity 0.792. Absolute alcohol is that which has been deprived of all water. Its specific gravity is 0.795. It eagerly absorbs water, and, as it becomes more dilute, its specific gravity rises; alcohol of 60 per



cent. has a specific gravity of 0.883. There are a number of forms of alcohol used in the arts. Alcohol, chemically considered, embraces a large class of similar bodies. Wood alcohol or methyl alcohol is made from the products of wood distillation, is a colorless mobile fluid with specific gravity of 0.80 and a boiling point of 150 degrees F. and is poisonous. It is a good solvent for many resins, but dissolves Pontianak resin scarcely at all. Some of the resins of other rubbers are attacked slightly by it. Grain alcohol is the product of the fermentation of starch or sugar and in the United States is made largely from corn, rye, and molasses. It is chemically termed ethyl alcohol and is the next in series above wood alcohol. Its boiling point is 170 degrees F. and its solvent powers for rubber resins is greater than that of wood alcohol, but some other resins are less soluble in the grain alcohol. It can be brought to a purity of only 96 per cent. by ordinary distillation, and this grade is known as cologne spirits or neutral spirits. Dissolves readily in benzol but not in petroleum benzine except slightly. Dissolves fatty acids but not fats or fatty oils except castor oil. Soluble in most rubber solvents or dissolves them. Grain or ethyl alcohol is the most commonly used alcohol and is usually the one referred to unless others are specified.

*Denatured alcohol* is merely grain alcohol to which have been added small quantities of substances which render it poisonous and undrinkable. The most common formula for denaturing alcohol is 5 per cent. wood alcohol and  $\frac{1}{2}$  per cent. petroleum naphtha or gasoline. Many other special formulas are allowed. When so denatured it may be removed from the distillery without the payment of the government tax.

*Fusel oil* consists of higher alcohols and is obtained in the manufacture of grain alcohol. It is insoluble in water and a solvent of many gums, and of pyroxylin or celluloid. Other substances, for example, phenol and glycerine, are chemically alcohols, but are not so called in commerce.

None of these really are solvents of rubber, but are frequently and largely used in varnishes. India rubber solution, when treated with large quantities of alcohol, is deposited in a spongy form, the foreign ingredients in the gum going into the

solution. Treated in this way it can be made an exceedingly white mass. It is also used in treating many of the pseudo-guttas to dissolve out the brittle resinous matter. It has also been claimed that the washing of raw rubber with alcohol dissolves resinous ingredients which are better absent, and that the rubber as a result lasts longer. Rectified spirit is what is generally used in connection with india rubber. It is used by the gatherers to coagulate the latex of the balata, and is used also in the production of resinolines (which see). One of the early uses was to mix with it various solvents—for instance, with spirits of turpentine, coal oil, bisulphide of carbon, ether, chloroform, etc. When ill-smelling solvents were used, it was also often incorporated to neutralize the odor. Dental and other gums are exposed to the sunlight in alcohol to increase the brilliancy of the colors and to make the shades lighter. Alcohol is also used to soften vulcanized rubber when a surface color is to be added. Alcohol, in connection with nitric acid, spirits of turpentine, and aniline, was used by Kelly for surface work on india rubber.

BENZOL, BENZOLE OR BENZENE is a volatile oil obtained in the distillation of coal tar, which must not be confused with petroleum benzine or petroleum naphtha. Its specific gravity is 0.899 at 32 degrees F., and 0.878 at 68 degrees F. Chemically it consists of 6 parts carbon and 6 parts of hydrogen. It is the basis for the manufacture of aniline dyes and many other coal tar derivatives used in the arts. It is the basis of nitrobenzene and aniline, the coal-tar colors. Commercially it is sold as pure, 90 per cent. and 70 per cent. By 90 per cent. benzol it is meant that 90 per cent. will distil over at the temperature of boiling water and likewise with 70 per cent. The commercial benzol is to a great extent obtained from the gas produced in the distillation of bituminous coal in the by-product coke oven. The commercial article is a mixture of benzol with higher boiling bodies which are very similar in their chemical properties, and these bodies are mostly toluol or toluene, which boils at 232 degrees F. and xylol or xylene, which boils at 287 degrees F. and higher boiling homologs. It is slightly soluble in water, and freely soluble in alcohol and ether, and in bisulphide of carbon. It has great solvent properties. Benzol is used largely as a solvent for rubber in manufacturing tire and inner tube cements.

Benzol is superior to carbon bisulphide as a solvent for chloride of sulphur and therefore is much used in the cold vulcanization process for curing light coated fabrics and thin, pure rubber goods. For this purpose benzol has the advantage of greater cheapness both as to price per gallon and as to lesser loss in handling than carbon bisulphide. This refers more particularly to the high grades of benzol, like 100 per cent. or C. P.; the 160 degrees benzol is mostly used where a solvent is required that must not evaporate too rapidly. It is said that if gutta-percha is put in 20 times its weight of boiling benzol, to which one-tenth of plaster is added, and the mixture agitated from time to time, a perfectly clear solution may be decanted. This is then mixed with twice its volume of 90 per cent. alcohol and the gutta-percha precipitated a pure white.

CAMPHENE is a name applied to one of the varieties of spirits of turpentine, which was once largely used as a burning fluid. It is very volatile, and the vapor makes with the air an explosive. Specific gravity 0.848. Camphene was formerly used to a certain extent as a solvent for india rubber. Under Newton's method of recovering rubber, the waste was placed in a closed vessel, covered with camphene, and heated to 158 degrees F. for fourteen days. The solvent was then distilled off, and the tough mass remaining was capable of utilization, and was somewhat similar to unvulcanized rubber. It was also used in boot-heel cements in the old-fashioned method of attaching them to rubber boots, and also in general shoe cements and in varnish for rubber footwear. Camphene was likewise used in putting vulcanized waste, finely powdered, into a solution in connection with ether and alcohol, in a simple but somewhat expensive process of recovery.

CAMPHOR has been used as a solvent for utilizing the waste of vulcanized rubber and of hard rubber, the waste being first treated with any ordinary solvent and then placed in a still with a certain amount of camphor, when the india rubber is dissolved and the solvent passed out and distilled over again. Granulated camphor, over which had been passed sulphurous acid gas until it was reduced to a liquid, was used also as a solvent for india rubber, by Alexander Parkes. Specific gravity 0.990.

CAOUTCHOUCINE, also spelled caoutchine, is a crude oil of india rubber, made by its dry distillation, and smelling much like naphtha. It is an excellent solvent for india rubber, but of course is too expensive for ordinary use. India rubber immersed in it swells exceedingly, and a considerable quantity of it is dissolved during the boiling. It must be kept in hermetically sealed vessels, as it has a great affinity for oxygen, which it absorbs energetically. In preparing it, the india rubber is treated in a retort at a heat exceeding 400 degrees F. Caoutchoucine dissolves in ether or alcohol, and, absorbing oxygen freely, forms a resinous body as a result. Specific gravity 0.650.

CARBON BISULPHIDE.—This excellent rubber solvent is a chemical prepared by the direct combination of carbon and sulphur under the influence of high heat. It is a colorless liquid, the specific gravity of which is 1.27. Its great volatility at ordinary temperatures makes it a most rapid dryer. When mixed with air and heated to 150 degrees C. it will explode. Its usual bad odor is due to sulphureted hydrogen and the presence of foreign matters, from which it can be thoroughly freed by purification. It is highly inflammable. It is a good solvent and has great affinity for sulphur, 100 parts dissolving 37 parts of sulphur cold, or 94.5 parts at 100 degrees F. Bisulphide of carbon mixes with every known substance capable of vulcanizing rubber. It also assimilates rapidly with all fatty oils, and dissolves all the resins, with the exception of shellac. It does not dissolve vulcanized rubber, however. Where it is used in rubber factories care is taken, as a rule, to remove the fumes, as they are injurious to the workmen. Some very serious cases of chronic poisoning have occurred through the use of this solvent, the symptoms being numbness, partial paralysis, and, in some cases, temporary insanity. The use of bisulphide of carbon in rubber factories is very carefully watched, therefore, by the authorities in Europe, proper means for ventilation and carrying off the fumes being insisted upon, and minors being excluded from rooms where it is used. It is one of the best and most common solvents for india rubber, very largely used in the Parkes cold curing and similar processes, and in cements.

CARBON BISULPHIDE SUBSTITUTE, a liquid produced by Dr. Carl Otto Weber, is said to be a perfect substitute for bisulphide



of carbon. It has these advantages: less chloride of sulphur is needed, the smell of the vulcanized product is sweeter, the vulcanizing solution penetrates deeper into the rubber, the risk of burning the rubber and uneven vulcanization are also done away with. It is also said that this substitute is not injurious to health. It is manufactured in England.

CARBON TETRACHLORIDE is a heavy, colorless, transparent mobile liquid, having a neutral reaction. Its odor is agreeable, but poisonous, resembling that of chloroform. It is non-inflammable and non-explosive. The vapors do not support combustion, but act as a fire extinguisher. The specific gravity of carbon tetrachloride is 1.6; the boiling point 77 degrees C. or 170 degrees F. The liquid is insoluble in water, diluted alcohol containing less than 75 per cent. by volume of absolute alcohol and also in glycerine and the glycerides. It is freely soluble in acetone, glacial acetic acid, oleic acid, liquid carbonic acid and aqueous solution of carbolic acid, ethyl, and amylic alcohol, chloroform, carbon disulphide, benzol, ether and aniline, oil of turpentine, petroleum and all petroleum products, also in fixed and volatile oils and oleoresins.

It dissolves oils, fats, resins, wax, india rubber, gutta-percha, cerasin, spermaceti, paraffin, stearine, varnish, asphaltum, pitch, balsams, coal tar, pine tar, and soda and potash soaps. It also dissolves salicylic acid, carbolic acid, iodine, bromine, iodoform, bromoform, menthol, thymol, camphor, camphor monobromate, naphthalene, etc. It also dissolves several gases, among others ammonia and hydrogen sulphide. It is not acted upon by the strong mineral acids and is not decomposed by an aqueous solution of potassium hydroxide, which will, however, remove any carbon disulphide or hydrogen sulphide present.

It is strongly recommended as an extracting medium. It is important to remember that in contrast with benzine, gasoline, etc., carbon tetrachloride ( $\text{C Cl}_4$ ) is a simple chemical compound, and in its recovery from the extracted fats, grease, etc., it is always obtained as the same chemical combination, with constant properties; whereas in benzine or gasoline there are unavoidable losses to be sustained, particularly the valuable, very volatile parts, so that with a continued use of benzine the remaining less



valuable ingredients, the heavier oils, must finally be enriched by important additions of fresh benzine or gasoline.

An apparatus installed for the recovery of the solvents does not need to be remodeled for the recovery of carbon tetrachloride, and the distillation process may be likewise carried through in the customary manner. Carbon tetrachloride does not in the least affect the colors of fabrics. The most delicate colors, even aniline colors of silk, satin, laces, etc., are not affected in the slightest degree. A mixture consisting of equal parts of turpentine and carbon tetrachloride cannot be ignited at ordinary temperatures. A mixture of 60 per cent. carbon tetrachloride and 40 per cent. naphtha is likewise non-inflammable at ordinary temperatures.

CHLOROFORM is prepared generally by distilling together a mixture of grain alcohol with bleaching powder and water. Its specific gravity is from 1.496 to 1.498. It is one of the best rubber solvents known. It is costly, however, and it should be remembered that a small percentage of chloroform in the air, even as little as 5 per cent., is dangerous to the workmen. Lascelles-Scott mentions what he calls the A. C. E. mixture, composed of alcohol 15 parts, chloroform 38 parts, and ether 47 parts, which yields a powerful solvent for india rubber or gutta-percha. Chloroform dissolves not only india rubber, but fats, resins, sulphur, alkaloids, and many other organic compounds. Chloroform is used as the solvent for india rubber which is treated with the ammonia gas process for bleaching. It is also used alone, and in connection with naphtha for rubber cements, which are intended to adhere to glass. In the bleaching of gutta-percha, it is also used as a solvent. One of the first uses of chloroform in connection with india rubber is to be noted under an American patent granted to Charles F. Durant.

CHUTE'S RUBBER RESIN SOLVENT.—This is a mixture of methyl acetate with either acetone or methyl acetone. Patented in the United States in 1907.

DICHLOR-ETHYLENE is a non-inflammable, non-poisonous solvent, of German origin. Its specific gravity is 1.269, with a boiling point of 181 degrees F.

DIPPEL'S OIL OR BONE NAPHTHA.—A thick, viscid oil of

brown color and very disagreeable odor, of specific gravity 0.970. On distillation it may be obtained limpid and colorless. It is prepared by the destructive distillation of bones, leaving bone-black as a residuum. It is chiefly used to make lampblack. It was one of the early solvents used for india rubber.

ETHER.—This was one of the early solvents used in connection with india rubber. It is sometimes erroneously called sulphuric ether. It is prepared usually by distilling a mixture of alcohol and sulphuric acid, washing the distillate, and rectifying the product with quicklime. It is a colorless, very mobile liquid, with a not unpleasant smell and is very volatile. Its specific gravity is 0.7183. It is soluble in water 1 to 12. Commercial ether boils at 96 degrees F., and yields a dense vapor. It is very inflammable, and when mixed with air or oxygen, gives rise to a dangerous explosive mixture. It is one of the best solvents known for oils and fats, and is also an excellent solvent for sulphur. For use in rubber work ether should be free from water, but not absolutely pure, necessarily. It is little used today in rubber mills, except in some lines of very fine work. It has the advantage of being absolutely free from the objectionable odors that many solvents have. A little is sometimes added to naphtha to make a complete solution of india rubber. There are also certain processes, expensive ones to be sure, for treating perished rubber with ether vapor to recover it. Ether was used to remove sulphur from vulcanized india rubber waste in Newton's camphene process.

ETHYLENE CHLORIDE OR "DUTCH LIQUID" has a specific gravity of 1.25.

GASOLINE.—See Naphtha.

HEPTANE.—One of the four isomeric hydrocarbons of the paraffin series, which occurs as a colorless liquid and is derived from heavy cannel coal oil, petroleum, etc. Its specific gravity is 0.712. It is soluble in alcohol and in ether, and is used with paraffin wax and india rubber in water-repellent compounds.

ISOPRENE.—A body found in oil of caoutchouc. It boils at 98.6 degrees F., and possesses the property of absorbing quantities of oxygen when exposed to the air, in consequence of which it forms an elastic, spongy mass. Specific gravity 0.682.

Isoprene is obtained by the action of moderate heat on oil of turpentine and is interesting as a basis for obtaining synthetic caoutchouc by polymerization.

The presence of isoprene formed in a reaction of a diolefine with conjugated linkings is detected by Ivan Ostromyslensky by shaking 5 to 10 drops of the products of the reaction for a short time with 50 cc. of concentrated aqueous sulphur dioxide solution, the mixture being then left at the ordinary temperature in a hermetically sealed vessel. In the course of 2 to 30 hours an abundant, colorless, amorphous precipitate is formed. This consists of a compound of the diolefine with sulphur dioxide possessing characteristic properties.

Isoprene may be determined quantitatively by converting it into 1.3-dichloroisopentane. If  $a$  grams of the dichloroisopentane compound be obtained from  $S$  grams of the crude isoprene, the latter contains  $3403 a \times 70.49 S$  per cent. isoprene. The procedure is as follows: 200 grams of the crude isoprene, containing butylenes, amylenes, benzene, etc., with boiling point 86 to 104 degrees F., is energetically shaken with 1500 cc. of fuming hydrochloric acid for 6 hours in a mechanical shaker. The black, opaque upper layer of chloro-compounds is separated, washed with aqueous sodium chloride solution saturated in the cold, again separated after the emulsion formed has separated into two layers, dried over calcium chloride and distilled. At 104 to 122 degrees F. only two or three drops of hydrocarbons generally distil over, and the fraction 122 to 194 degrees F. contains butylene and amylenes chlorides. The fraction 194 to 266 degrees F. is collected separately. From 266 degrees F. the temperature usually jumps immediately to 288 degrees F., the boiling point of the 1.3-dichloroisopentane. When the crude isoprene has been obtained, for example, from turpentine, the 1.3-dichloroisopentane cannot be distilled, but it is found that the residue distilling with boiling point beyond 291 degrees F. consists, in spite of its black color, of almost chemically pure 1.3-dichloroisopentane. This residue may be filtered through glass wool and the filtrate weighed. The fraction boiling at 194 to 266 F. is subjected to careful fractional distillation, as it contains 1.3-dichloroisopentane, sometimes in considerable quantity.

The fractionation is carried out three times in each case up to 288 degrees F.

**METHANE.**—Professor Lascelles-Scott describes the manufacture of what he calls methane solvents, which are really benzenes or benzols through which marsh gas has been passed. He claims that a benzene containing from 2 to 3 per cent. of methane, obtained in this way, yields a better and more mobile solution than the ordinary solvent naphtha, and the solution when spread dries off better, besides giving a more finished surface.

**NAPHTHALENE.**—Commercially obtained from coal-tar, being among the third and fourth products of the distillation of that body. Naphthalene is often sold in balls made by melting the large silvery plates or scales in which it crystallizes, and running the melted compound into molds. Its specific gravity is 1.15. It is insoluble in water and petroleum naphtha, but the liquids derived from coal tar dissolve it easily. Naphthalene is sparingly soluble in alcohol and ether, but readily in benzol. It is used in insulating paints, as when it evaporates it leaves a very solid film that is said to be absolutely free from porosity.

**NAPHTHA.**—The term naphtha was originally applied to a variety of pungent, volatile, inflammable liquids that belonged chiefly to a class of ethers; then it took in oils of natural origin, such as rock oil, petroleum oil, etc.; at a later date, a light oil of coal tar, which should properly be designated benzol, was included under the name of naphtha, while recently it has been extended so that it covers most of the inflammable liquids distilled dry from organic substances. It is applied in the United States to a series of hydrocarbons that are obtained from petroleum, whose boiling points vary with the densities, from 65 to 300 degrees F. The naphthas of commerce are bog-head naphtha, obtained from bog-head coal; bone naphtha, or Dippel's animal oil; coal naphtha, obtained from the distillation of coal tar; wood naphtha, or methyl alcohol, obtained during the dry distillation of wood. Of these, coal-tar naphtha and petroleum naphtha are most useful to rubber manufacturers. The former of these was used largely as a rubber solvent, but today it is almost wholly replaced by petroleum naphtha.

*Petroleum naphtha* is a general name embracing a series of light distillates from crude petroleum. In the order of their lightness of gravity and boiling points the petroleum naphthas are: rhigolene (specific gravity about 0.665), gasoline (specific gravity 0.665), benzine (specific gravity 0.680-0.700), and ligroïn.

The distinction should be noted between the petroleum distillate "benzine" and the coal-tar distillate "benzene" or benzol.

*Ligroïn* is a naphtha similar to benzine, used as a burning fluid in the ligroïn or "Wonder" lamp.

These products evaporate rapidly in a current of warm air and form explosive mixtures with the air.

*Coal-tar naphtha* was one of the first solvents used in rubber work. Macintosh, as far back as 1823, prepared it himself for dissolving india rubber for proofing. There is obtained from crude coal-tar naphtha what is known as "once-run" naphtha and "last runnings." The once-run naphtha is the starting point from which are derived the various grades of benzols, solvent naphthas, etc., by fractional distillation. The specific gravity of solvent naphtha should not exceed 0.875. Its composition is very complex, including xylols, cumols, homologs of benzol, together with some paraffin, and sometimes a little naphthalene. This last-named substance is often objectionable, as it acts upon some rubbers like animal oil. Naphtha derives its vegetable solvent power largely from the xylol present in it. This is today removed and sold by itself as a solvent, though the residual naphtha is proportionately reduced in value.

Lascelles-Scott, after exhaustive experiments, thus describes three naphthas used in England in rubber factories. Petroleum naphtha in its solvent action on rubber showed slight action in the cold or under gentle heat. Viscid masses and semi-solutions were formed, but these solutions did not dry well. The same naphtha had almost no solvent action on pitch. Shale naphtha was useful only in dissolving Madagascar rubbers, and had no action on pitch, while coal-tar naphtha caused almost any rubber to swell quickly and, after gentle heat, effected a good solution. It also readily dissolved pitch, forming a deep-brown solution.

The problem that confronts rubber manufacturers as a rule is the solution of gums that are more or less heavily com-



pounded, which is an easier problem than the solution of crude rubber that perhaps has not been broken down in any way. At the same time it is customary in many cases to apply a little heat during the mixing. The following table relates to petroleum naphthas. The *C* naphtha has not only the greatest solvent power, but it is easier to evaporate after it has dissolved the rubber compound. *B* and *A* require a certain amount of heat to vaporize them:

Products.	Specific Gravity.	Degrees Baumé.	Boiling Points.
Rhigolene .....	0.625	..	65 degrees F.
Gasoline .....	0.665	85	120 degrees F.
<i>C.</i> Naphtha .....	0.706	70	180 degrees F.
<i>B.</i> Naphtha .....	0.724	67	220 degrees F.
<i>A.</i> Naphtha .....	0.742	65	300 degrees F.

Naphtha is more largely used in the proofing business than any other solvent. It is a general solvent for cements, and quantities of it are used in almost all lines of rubber work where there is any making up of separate pieces after calendering. It is therefore necessary that a good grade be used in consideration of the danger that may come from fires caused by the explosion or easy ignition of low-grade solvents. Odorless naphthas are those from which naphthalene, a solid white body, has been removed, as it is the presence of this body that causes the strong smell. Naphtha treated by sulphuric acid acquires a rather pleasant odor as a consequence. It is often mixed with other solvents—for example, with oil of turpentine—and is found thus to have a better solvent effect on the rubber.

PENTANE.—A hydrocarbon of the paraffin or methane series. A colorless, volatile liquid which occurs in petroleum. Boiling point 98 degrees F. Pentane is used with paraffin wax and india rubber in water-repellent compounds. Specific gravity 0.645.

PETROLEUM SOLVENTS.—The petroleum oils are by far the cheapest oils in commerce. They are solvents for rubber and are more extensively used for that purpose than any other class. In defining petroleum oils it is hard to make definite distinctions, for every oil is a mixture of many separate chemical substances, and the names used to designate them in the trade and the tests used are indefinite and the products of no two manufacturers agree in name or test.

Petroleum oils consist in the main of hydrocarbons of several series, and a large number of each series is found in each kind as it is taken from the ground.

The first oils obtained from Pennsylvania and West Virginia consisted of oils of the paraffin series exclusively, having the general formula  $C_nH_{2n+2}$ . This series begins with marsh gas with one carbon atom and goes up to the paraffin waxes with many carbon atoms in each molecule, but each compound has the same ratio of carbon and hydrogen as pointed out above.

When this oil is distilled there first passes off a little marsh gas which is dissolved in the oil, and following this is a series of products up to pentane, which boils at 36 degrees C., which are mostly lost, though products are sometimes made which will remain liquid only under pressure and will rapidly evaporate in the air. For example, there is a product known as cymogene which boils at the temperature of melting ice and has a specific gravity of 110 Bé., and the next higher product is known as rhigolene, which boils at about 65 degrees F., or ordinary temperature, and has a specific gravity of 100 Bé. Sometimes a product known as petroleum ether, boiling between these points, say about 50 degrees C., is made.

The next product obtained by distillation of Pennsylvania oil is petroleum ether of 85 degrees Bé., or gas-machine gasoline, which is very scarce now. It begins to boil at about 50 degrees C. and contains some that boils at 120 degrees C. This is sometimes called benzine, but must not be confused with the coal-tar benzene or benzol.

Then there are a series of gasolines of different gravities and boiling points. It was customary to use gasoline of 76 degrees Bé., but this product is now almost unobtainable, and that of 66 Bé., with a boiling point ranging up to 140 degrees C., is largely used. After these products come the kerosenes, or burning oils, which are not volatile enough to be used for solvents which have to be later evaporated.

The petroleum trade has clung to the use of the Baumé hydrometer as a standard for grading oils, and usually no other characteristic of the oil than its Bé. gravity is used in the trade. While all the oil used was of the paraffin series, the Bé. gravity

was an indication of its relative volatility. This is now of no value when other hydrocarbons are present.

When the oil of Pennsylvania became exhausted the oils of Ohio assumed great importance, and these were found to differ in many respects. While the oil of Pennsylvania was of a dark greenish-red of from 49 to 34 Bé., it was quite mobile and rather transparent, and had no impurities, such as sulphur or other objectionable matter. The Ohio oils were found to contain large quantities of sulphur and required special treatment, and there were in them other hydrocarbons than the paraffins. Now these other hydrocarbons which correspond in boiling point with the paraffins have different specific gravities and are usually heavier, so that a gasoline or naphtha from them of a heavier gravity, say 70 Bé., might have as low an average boiling point as one from Pennsylvania oil of 76 Bé. As the products of the fields of Illinois, Texas, California, Wyoming, and Oklahoma came into the market in turn, it was found that these oils consisted largely of other series of hydrocarbons and that in many cases they contained an asphalt base instead of a paraffin base. Many also contained much sulphur and some contained little or no gasoline or naphtha.

These oils from the western part of the United States contain large amounts of oils of the olefine series and some of the acetylene or aromatic series. The latter, while having a different gravity from the paraffin series when of the same boiling point, are as good for rubber solvents as the paraffin hydrocarbons, and indeed often better.

In purchasing petroleum naphthas, therefore, at the present time it is not sufficient to ask for a naphtha of a certain gravity, but it must be examined and tested as to its boiling point first. If the oil begins to distil too low it is rather dangerous, as it will be more inflammable; that is, the vapors given off at ordinary temperatures will ignite easily and will carry a long way from their source and will explode if they come into contact with a light or flame. If there is much of a residue which distils only at a high temperature, the solvent will be too slow in drying and the rubber dissolved in it may remain tacky. The naphthas should also be tested for their dissolving power, as it may vary widely, according to the hydrocarbon series present.

Rubber manufacturers have been confronted for a number of years with constantly rising prices for naphthas, and a constantly poorer grade has been received. This situation had no connection with conditions in the rubber trade, but was due to the enormous increase in demand for gasolines for motor vehicles.

**PINE OIL.**—This is made by distillation from dead wood of the Scotch fir (*Pinus sylvestris*). It has an unpleasant empyreumatic odor. This is fatal to its use when it appears in the finished goods, but when it is removed the odor can be tolerated in the workrooms, with proper mechanical ventilation. Pine oil is also made from wood at the same time as turpentine, and is a less volatile compound. Both of these oils will dissolve rubber better than petroleum naphthas and as well as coal-tar products.

**PROPYLENE CHLORIDE.**—The specific gravity is 1.165 and the boiling point 207 degrees F.

**RHIGOLENE.**—See Naphtha.

**ROSIN OIL.**—This is obtained by subjecting rosin to dry distillation, the specific gravity of the resultant oil ranging from 0.96 to 0.99. It is rarely used as a solvent for rubber, in the ordinary meaning of the term. As a matter of fact, it is not a good solvent for crude rubber. For compounded rubbers, however, it works well and is often used, particularly in connection with pseudo-guttas. In certain insulating experiments, where a thin sheet of gutta-percha covered the conductor, and the outer gutta-percha tube was full of rosin oil, it gave, according to Professor D. E. Hughes, F.R.S., a higher insulation test than gutta-percha alone. Professor Hughes used rosin oil quite thick and viscid, and added resin and a solid residuum obtained from the distillation of palm oil. Rosin oil in rubber compounding, however, softens the compound in a marked degree.

**SHALE SPIRIT** is the solvent used in the Scottish waterproofing establishments. It is a product of the Scottish paraffin oil industry.

**TETRACHLORIDE OF CARBON.**—See Carbon Tetrachloride.

**TETRACHLORMETHENE BENZENE SUBSTITUTE** is an excellent solvent, boiling at 75 degrees C. Not easily ignited; of pleasant smell; made from chlorine and carbon bisulphide.

THION.—A substitute for bisulphide of carbon, manufactured in England, said to mix excellently with chloride of sulphur, and is non-poisonous.

TOLUOL OR TOLUENE.—That oil which is distilled from coal tar at a temperature of 230 degrees to 234 degrees F., also called methyl benzene and toluole. Specific gravity 0.872. It resembles benzene in outward appearance. Much commercial benzol contains toluene, which makes it a far better solvent for rubber than benzene itself, as it dissolves the rubber in five-sixths of the time. The solutions are more mobile; it has a higher boiling point; and, given a quantity of the solvent, will dissolve more gum even at low temperature. It leaves a more solid deposit of rubber than benzene, and does not induce headache or sickness.

TURPENTINE (crude) is known as an oleo resin, and is of about the consistency of fresh honey. There are more than a dozen varieties on the market, the more common being Bordeaux, Venice, Canadian, and American. A fair quality of turpentine oil should begin to boil at 155 degrees C. or 311 degrees F. The distillation of crude oil of turpentine by steam leaves ordinary rosin. Oil of turpentine is used in certain waterproof cements, in connection with both gutta-percha and india rubber. Where oil of turpentine is necessary for rubber work, it is well to have it free from the considerable percentage of water which it invariably contains. This is done by a treatment with sulphuric acid, or by rectifying it over burnt lime. Turpentine, particularly that known as Venice turpentine, is often used in connection with linseed oil and sulphur in the production of rubber substitutes. Professor Tilden showed, some years ago, that what appeared to be pure india rubber could be obtained from turpentine; indeed, he announced that he had produced it on a small scale. The same thing was also observed by Boucharadat. Venice turpentine is obtained from Switzerland, where it is procured from the *Larix Europea*, or larch. The genuine Venice turpentine is of the consistency of honey, cloudy, yellowish, or slightly greenish. It is entirely soluble in alcohol. The commercial Venice turpentine is a factious substance, usually quite brown, and is prepared by dissolving rosin in oil of turpentine. Venice turpentine is largely used in cements. Bor-



deaux turpentine is the ordinary turpentine of commerce, getting its name from the port in France whence it is exported.

TURPENTINE OIL OR SPIRITS OF TURPENTINE has a specific gravity of 0.864. It is colorless, transparent, with strong odor, and bitter taste. It is insoluble in water, on which it floats, but readily soluble in strong grain alcohol, ether, and the fixed and essential oils. It is an excellent solvent for sulphur, resin, and india rubber. Spirits of turpentine, with wood spirit alcohol, aniline, and nitric acid is used in surface work on vulcanized india rubber. The earliest records of india rubber speak of this oil as a solvent; indeed, the whole secret of rubber compounding for a number of years, when the great Roxbury Rubber Co., of Boston, was running, was the solution of india rubber in turpentine. It is used in solutions that are expected to be sticky, and to dry slowly.

VULCOLEINE is a liquid of English origin, and is put upon the market at about the same price as carbon bisulphide, and used for a solvent for india rubber. It leaves on evaporation a perfectly tough and elastic film, quite unlike that left by coal-tar naphtha, or the usual solvents. It mixes instantly with chloride of sulphur, and is intended to replace bisulphide of carbon in the cold-curing process. It has no bad smell, nor is it unhealthful.

WOOD SPIRIT.—See Alcohol.

XYLOL.—A colorless, somewhat aromatic, inflammable, oily liquid distilled from coal tar and wood tar; also called xylene. It is similar to benzol and toluol. Specific gravity 0.882.

## CHAPTER XIV.

### MISCELLANEOUS PROCESSES AND COMPOUNDS FOR USE IN THE RUBBER FACTORY.

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#### SURFACE COLORING AND PRINTING.

THE formulas given below for the dyeing and surface coloring of rubber, although interesting, are not such as will generally be used.

A suggestion for coloring that comes from France is the dipping of rubber for an instant in a bath of nitric acid, then washing in water. Next, the rubber is dipped for coloring in an alcoholic solution of fuchsine. The experimenter should appreciate fully, however, the effect that nitric acid produces on rubber, and govern himself accordingly.

Alexander Parkes, who produced some exceedingly valuable processes for the treatment of rubber, gives the following formulas for dyeing india rubber:

*Black*.—Boil from 15 to 30 minutes in a liquid prepared as follows: sulphate copper, 1 pound; water, 1 gallon; caustic ammonia or muriate of ammonia, 1 pound. Or: sulphate or bisulphate potash, 1 pound; sulphate copper, 12 pounds; water, 1 gallon.

*Green*.—Muriate ammonia, 2 pounds; sulphate copper, 1 pound; caustic lime, 4 pounds; water, 1 gallon. Boil the rubber as before, 15 to 30 minutes.

*Purple*.—Sulphate or bisulphate of potash, 1 pound; sulphate of copper,  $\frac{1}{4}$  pound; sulphate of indigo,  $\frac{1}{4}$  pound. Boil the rubber, 15 to 30 minutes.

Hoffer gives almost the same ingredients for producing these colors, adding the information that the articles are dyed by being boiled in these fluids from 15 to 30 minutes, the thicker the article the longer the boiling. This is done before the goods are vulcanized.

Hard rubber may be decorated by means of pigments mixed with shellac and applied to the given surface with a brush. The surface then is to be pressed with some force against a hot plate of metal, whereby the colors are made to appear as though integral with the rubber.

Wood coated a sheet of vulcanized rubber with chloride of silver, the idea being to use it in dental plates. Various processes have also been brought out for the surface treatment of rubber with gold leaf, bronzes, etc., usually applied in the form of powders, in the manner in which flock (powdered fiber) is applied. Truman also patented a process for electro-gilding rubber dental plates after they were finished.

Goodyear dusted unvulcanized rubber surfaces with plum-bago or powdered metal, to make them electrically conductive, pressed the dust in, and then electroplated upon it.

The embossing of india rubber surfaces has been practiced almost since the invention of Goodyear's "triple compound." It is really nothing more than a light surface molding. This is done sometimes by embossing rolls, the rubber being cured after the impression is taken, and sometimes by being vulcanized on the impression plate.

Bourbridge patented a process for embossing rubber by rolling it tightly on a drum with embossed paper or bookbinders' cloth, and semi-curing it in that form, preferably by boiling in water at a temperature from 212 degrees to 220 degrees F. This boiling operation was not really vulcanization, but simply a means of setting the rubber, which was afterward made up into goods and cured.

In producing sheets of india rubber for the manufacture of tobacco pouches, balls, balloons, etc., by this process, the sheet is calendered on sized cloth, partially vulcanized, printed, coated with transparent india rubber, the goods made up, and the vulcanizing process completed.

Printing on inflatable thin rubber films, such as toy balloons, may be neatly done by applying the inflated article to the inked type or electrotpe.

A great many beautiful colors are added to india rubber surfaces by coating the sheet with a thin adhesive solution, dusting it over with colored flock, and then vulcanizing. By this

process any color can be given to rubber surfaces which are to have a cloth-like appearance.

Kelley produced a bronzed appearance on rubber-coated fabrics by means of a roller partly immersed in a trough holding the dye, curing either by dry heat, or by chloride of sulphur. His solution consisted of 2 ounces alcohol spirits, 1 ounce wood naphtha, 10 drops nitric acid, 1 ounce spirits of turpentine (with sufficient aniline dye to make the desired color), 4 ounces liquid dyeing, 3 pounds rubber composition. He also impregnated farina with aniline solutions, dried it, and mixed it in the compound.

In certain dyeing processes lakes are necessary. A caoutchouc lake is made by steeping 1 ounce of Para rubber in a quart of light camphor oil, exposed to the sunlight for several days. This is said to be excellent for binding colors.

Matthew's process for producing colored designs for proofed fabrics is to first coat the fabric in the ordinary manner with pure or colored india rubber. When the design is to be printed on a black or dark ground, the last coating is mixed with starch or some powder that will render it non-adhesive, and to an extent absorptive. The fabric is then partially vulcanized, when the designs are printed on the desired surface. The vulcanization is finished preferably by using chloride of sulphur.

Colors suitable for admixture with rubber should answer the following requirements: they must be unaffected by water, acids, alkalies, or chloride of sulphur. Further, they must not be affected by sulphur at temperatures ranging from 200 degrees to 300 degrees F. The colors must not be soluble in or affected by naphtha or other solvents used in rubber work. According to Frankenburg, his invention of aniline lakes answers all these requirements. His description is as follows:

(A.) Lakes prepared from acid aniline colors.—“I have found that by converting any of the acids or suphonated aniline colors into compound lakes, such as barium-alumina, calcium-alumina, barium-chromium, or calcium-chromium lakes, colors are obtained answering all the above requirements, and therefore eminently suitable for the dyeing of india rubber, water-proof, and other articles. The aniline dyes best suited for the production of these lakes are those known as azo or di-azo col-

ors. From colors of this description I prepare lakes in the following manner: 50 pounds of orange II., or any other suitable azo or di-azo color, and 112 pounds of soda crystals are dissolved in 100 gallons of water at 170 degrees F. This solution is then precipitated with a solution of 150 pounds of barium chloride. The precipitate is kept boiling for half an hour. It is then left to stand, and washed several times with fresh water. Eventually a solution of 40 pounds of alumina sulphate is added very gradually, when a bright, fast, and flocculent lake is obtained, which, after filtration, drying, and pulverizing, is ready for incorporation with the india rubber dough. It is evident that a great many variations of the process may be devised, but in every case the important point is the conversion of the aniline dye into one of the above-mentioned compound lakes. As regards the proportions given above, they are, of course, subject to such variations as are in accordance with the molecular weights and the commercial purity of the materials used, as well as with the particular properties and qualities to be imparted to the lakes for the purpose they are intended to serve. Using in this manner the numerous azo and di-azo dyes a very great variety of lakes may be produced, comprising all conceivable shades, and all suitable for the dyeing of india rubber articles of every description. The lakes prepared from the acid oxy-ketone dyes and most of the natural dyes are very suitable for this purpose owing to their indifferent and dull shades."

(B.) Lakes prepared from basic coloring matters.—"A large number of lakes derived from this class of dyes are also suited for the dyeing of india rubber articles, although many of them are lacking in fastness to light acids and alkalis. To produce a perfect compound lake from these dyes tannic acid and antimony, along with aluminum and barium, are used for the complete fixation and precipitation of these lakes. The following proportions give good results: soda carbonate, 128 pounds; barium chloride, 110 pounds; thioflavine, 25 pounds; tannic acid, 20 pounds; acetate of soda, 20 pounds; sulphate of alumina, 100 pounds. These colors can be made faster by adding to them a small quantity of antimony potassium-tartrate. The proportions of tannic acid, sodium acetate, and tartar emetic used in this process vary considerably with the different basic colors, such



variations being due to the difference in the atomic weights and commercial purity of the basic dyes."

Hebblewaite and Holt's process for producing designs on gossamer cloth calls for spreading farina or other powder over the rubber surface, then running the fabric through embossed rollers and producing patterns thereon.

Mosley's ornamented fabric was a gossamer cloth covered with farina, the surface being printed much as calico is, and then vulcanized with chloride of sulphur. The colors were mixed with suitable solvents and a certain amount of paraffin or india rubber added. A part of this invention was also the use of an engraved roller, which revolved in the vulcanizing solution, and came in contact with the surface of the rubber, only at its raised portion. Directly after passing over the roller, the surface of the rubber was dusted with farina, which adhered to the portions that had come in contact with the roller, and not to the rest, thus producing a design on the fabric. The whole of the coating was afterwards cured by vapor.

IMPREGNATING RUBBER.—Lessnenn and Weinkopf advise the brush application of the following to prevent sun-cracking: Sixty per cent. birch tar oil; 38 per cent. coal-tar benzene; 2 per cent. dissolved dextrine.

#### SHOWER-PROOF PROCESSES.

THE Cravenette and other processes for rendering textile fabrics waterproof or water-repellent have attracted so much attention in the rubber trade that space will be given here to a description of the Wiley patent, which is used at the Cravenette Works, Bradford, England.

The waterproofing compound is applied in a solid or hard state by the action of friction and heating. No solvents are used, nor is it a calendering process. The advantage of this is a lessening in the cost of applying waterproofing solutions and a further valuable result is that the dyes on various fabrics are in no way disturbed, and no unpleasant odor is developed or imparted to the cloth. The substances chosen are those which have a low melting point, so that the fabrics are not damaged by heat. They are preferably ozocerite, stearine, spermaceti, paraffin wax, beeswax, or Japanese wax. These are sometimes used singly, and

sometimes in combination, considerable judgment being necessary in selecting those which have an affinity for or are readily absorbed by the fibers of particular fabrics, influenced also by the nature and color of the fabric. In some cases india rubber, gutta-percha, maltha, asphaltum, resin, and artificial gums are found valuable in small proportions, and in conjunction with the substances already mentioned.

In order to apply the waterproofing substance, it is formed into slabs. The fabric is carried on a reel supported in bearings between suitable frames, at the opposite end of which is a hollow cylinder mounted upon carrying rollers and supported laterally by side rollers. This cylinder is filled with water. The slab of the compound, wider than the fabric to be coated, is fixed in a holder above the cylinder. This holder is so arranged that the weight presses the slab against the cylinder. The fabric is then drawn from the reel over and under tension bars, under a supporting roller, between it and the rubber cylinder, and around the cylinder and under the slab, then over the guide roller and into a drying machine. The friction of the cloth wears the slab away and uniformly deposits it upon the cloth while in the drying machine, the heat melts the waterproofing compound, and it is absorbed by the fibers, which are thereby rendered waterproof or water-repellent.

Other formulas for shower-proofing and waterproofing are of interest in this connection and a few are given:

A German waterproofing compound: alum, 10 pounds; sugar of lead, 10 pounds. Dissolve in hot water and allow the precipitate to settle. Dilute the clear liquid with 120 gallons water and add 2 pounds isinglass in solution. The goods are steeped in this solution 8 or 10 hours.

An American shower-proof compound: liquid silicate of soda, 1 gallon; white oxide of zinc, 1 pound. If the fabric is to be colored, add coloring matters. The mixture may be applied to fabrics hot or cold, by means of a brush or by immersion of the fabrics, which are afterwards to be run between rollers.

Another American compound: dissolve separately,  $1\frac{1}{4}$  pounds alum (in hot water), 10 ounces acetate of lead (in hot water), and  $1\frac{1}{2}$  pounds carbonate of magnesia (in hot water). They should aggregate about 31 quarts. Add the acetate of lead

to the alum solution, and then the carbonate of magnesia; after which 10 quarts liquid as above and 1 tablespoonful white gum arabic. Stir  $\frac{1}{2}$  hour; let stand 24 hours, skimming now and then; in 48 hours the first mixture will be ready. Lay the fabric in a vessel and pour liquid over it, beating the fabric well and removing it within an hour.

A third American shower-proof compound:

- |    |   |                      |
|----|---|----------------------|
| A. | Carbonate of soda .....   | 16 parts.            |
|    | Lime .....  | 8 parts.             |
|    | Water .....   | 32 parts.            |
|    | Boil 30 minutes, let settle and pour off the clear lye.                   |                      |
| B. | Glue or gelatine .....  | 3 parts.             |
|    | Linseed oil .....   | 3 parts.             |
|    | Add after soaking glue in cold water 12 hours.                            |                      |
| C. | Tallow (or other animal fat) .....  | 16 parts.            |
|    | Rosin .....   | 8 parts.             |
|    | Melt together.  |                      |
|    | To (A) boiling hot add hot (C), then pour in (B)                          |                      |
|    | and stir hot until well mixed.  |                      |
| D. | Sulphate of alumina .....   | 1 pound.             |
|    | Acetate of lead .....   | $\frac{1}{2}$ pound. |
|    | Boiling water .....   | 8 gallons.           |
|    | Let settle and draw off clear liquor for use. To 1 gallon                 |                      |
|    | water add $\frac{1}{2}$ ounce of first product for bath for cotton goods. |                      |
|    | Add $\frac{1}{4}$ ounce for silk or wool. Immerse 24 hours or more, then  |                      |
|    | six hours or more in second compound (D).                                 |                      |

Proofing compound:

Mixture 1.—Dissolve in water, 50 parts alum; also dissolve in water, 35 parts sugar of lead; mix.

Mixture 2.—Combine 17 parts paraffin and 35 parts benzine; drop into this 17 parts caoutchouc. Stir until well dissolved.

Mixture 3.—To the clear decanted liquor from the above mixture, add 8 parts alcohol and 4 parts eau de cologne (or oil of lemon).

An English compound for waterproofing textile fabrics: sugar soap, 1 pound; water, 16 gallons. Soak articles in them for 6 hours; drain, but do not wring them; and place them in the following solution: alum, 1 pound; water, 16 gallons; soak again 6 hours, take out and dry without wringing.

Another English compound for waterproofing textile fabrics: concentrated size, 8 pounds; aluminum sulphate, 5 pounds; barium chloride, 6 pounds; water, 16 gallons. After coating, varnish with the following: Melt together 22 pounds colophony, 4 3-5 pounds crystallized soda, and 11 pounds water. Then add:

ammoniacal fluid,  $5\frac{1}{4}$  pounds; and water, 55 pounds; or: borax, 6 pounds; shellac, 6 pounds; and water, 40 pounds.

A German compound for waterproofing woollens: dissolve 100 pounds alum in moderate quantity of boiling water; soak 100 pounds glue till it has taken up twice its weight of cold water, then apply heat to dissolve it; stir 5 pounds tannin and 2 pounds soluble glass well into the glue, then add the alum solution. Enter the goods at 80 degrees C., and steep 30 minutes. Take out and drain several hours, stretch on a frame, and, when dry, calender.

A German shower-proof compound: stir 9 pounds casein well in 32 quarts water, adding little by little 25 pounds of slaked lime. Add a solution of  $4\frac{1}{2}$  pounds soap in 26 quarts water.

Filter and treat the cloth with the liquid. Dress with a dressing of acetate of alumina, by which the casein is rendered insoluble in the fibers of the cloth. After two applications, rinse the goods with hot water, press strongly, and dry.

One process for waterproofing threads and yarns used in weaving ducks and other fabrics is in two parts, the first of which relates to a tanning mixture in which the yarns are immersed, consisting of: birch bark, 14 pounds; bichromate of potash, 1 pound; chloride of calcium,  $\frac{1}{2}$  pound; tar, 1 pint; solution of alkali, 2 pounds. The threads are first boiled in a 5 per cent. solution of alkali to destroy perishable matter, after which they are immersed in the tanning liquid and dried. The second part consists of preparing or dressing the threads with the following compound: poppyseed oil, 2 gallons; india rubber solution, 2 pounds; red oxide of mercury, 1 pound; resin, 28 pounds; beeswax, 28 pounds; palm oil, 14 pounds. The threads after this treatment are wound on reels for weaving.

Forster, in 1847, made a water-repellent compound in which he used spermaceti, wax, and stearine, while three years prior to that Townsend used two solutions to accomplish that end, the first being water, calcined British gum, white soap, logwood liquor, and alum; the second being water, sulphate of zinc, calcined British gum, and palm soap.

The kyanized cloth process is well known in connection with preserving fabrics, the treatment being with a mixture of corrosive sublimate, chloride of zinc, pyrolignite of iron, oil of tar,

and resinous matters. Fabrics treated in this way have been used for the manufacture of hose.

According to Dr. Doremus the lightest fabrics are rendered unflammable by dipping them in a solution of phosphate of alumina in water.

Allard's fireproof felt is made of 50 per cent. of asbestos and 50 per cent. of animal hair, and for ordinary purposes is wholly fireproof.

Canvas for sails and other purposes, which it is desired to render waterproof, is treated by the Dumas process so that, while it is both waterproof and fireproof, it is still elastic and permeable by air. The treatment is this: The material is first put in a solution of gelatine, then run through pressure rollers, and spread in the open air to dry; later it is dipped in a cold solution of alum, again exposed to the air, then washed in cold water, and finally dried.

Frankenburg's waterproof cloth is made in this manner: Both warp and woof are coated in the yarn with india rubber, then powdered with farina, then woven, after which the fabric is calendered, and the result is a cloth that is thoroughly waterproof, and yet does not give evidence of having rubber in its make-up.

Smith's porous waterproof fabric called for a compound made of 100 parts of paraffin melted by heat, to which was added 15 per cent. of india rubber, the mixture being kept from 5 to 30 minutes at a temperature of 100 degrees C. The solution, either as it is, or with a solvent, is then transferred to the cloth by means of a set of rollers which have a temperature of about 70 degrees C.

AMPHIBOLINE.—A natural earth found in Germany, which once mixed with water, will not mix again. Used with a small amount of gelatine for waterproofing. Formula: 34 parts amphiboline, 9 parts gelatine, 2 parts chrome alum, 2 parts ammonium sulphate, 53 parts water.

Cohuru's waterproofing compound: This consists of crude petroleum, 3 quarts; liquid asphalt, 1 pint; white drier, 1 pint; beeswax, 4 ounces, and gum-arabic.



## DEODORIZATION.

THE odors that cling to vulcanized rubber goods and to gutta-percha are often very objectionable, and the following processes are given for deodorization:

Cattell's process: For every pound of well-cleaned gutta-percha take 15 pounds of the following solution: benzol, 1 gallon; alcohol, 1 ounce; glycerine, 30 drops. Or benzol, 1 gallon; nitrate of the oxide of ethyl, 30 drops; heat in a closed vessel to 110 degrees F. The gutta-percha is recovered by cooling to below 32 degrees F., and pressing or by distilling off the solvent, or by precipitation with fusel oil.

Freeley's process: dip vulcanized rubber goods in a solution of: salicylic acid, 20 grains; alcohol,  $\frac{1}{2}$  pint. This will deodorize them, but goods will be toughened and the deodorization increased by subjecting goods to a bath in hot or cold solution composed as follows:

(A) Oak bark, 50 pounds; hemlock bark, 50 pounds; sumac bark, 50 pounds; water, 900 gallons.

(B) Solution as above, 2 gallons; salicylic acid, 20 grains; large tablespoonful of Russian jackten extract, dissolved in 2 pints of alcohol, 1 pint of ether, and 10 grains of salicylic acid.

Bourne's process: The articles to be deodorized are placed between layers of charcoal and heated from 120 degrees to 150 degrees F., if unvulcanized; 180 degrees F., if partially vulcanized; or 212 degrees F., if completely vulcanized. Heat for six hours or more.

Lavater and Tranter's process: Subject the articles to a boiling in potash, then to a vacuum, then to a pressure of air scented with some essence. They claim the extraction of the sulphur from the pores of the rubber in the form of sulphureted hydrogen and its replacement by perfumed air.

Charles Hancock's process: To remove the odor of gutta-percha, steep it in the following solutions:

(A) Soda or potash, 1 pound; water, 10 gallons.

(B) Chloride lime, 1 pound; water, 10 gallons.

De la Granja's process:

Iodine .....	15 grains.
Pernanganate of potassa .....	20 grains.
Iodide of potassium .....	60 grains.
Glycerine .....	4 ounces.

De la Granja's process (*Continued*):

Sulphite of soda .....	4 ounces.
Sulphite of lime .....	4 ounces.
Sulphite of potassa .....	4 ounces.
Water .....	1½ to 2 gallons.

Soak rubber in a solution composed as above, in a close earthen vessel, 24 hours, the solution being cold. Then heat the solution gradually to boiling point and uncover the vessel until ⅓ of weight of solution evaporates. When the solution cools remove the rubber.

The Traun Rubber Co. patented a process for adding powdered perfumes to india rubber, the stock being used for dental dam, dress shields, and the like.

#### PRESERVING RUBBER GOODS.

THE deterioration of vulcanized rubber goods is often a serious matter, where it is necessary for some time to keep them in store. Wherever possible, they should be kept in a cool, dark place, and away from warm currents of dry air, and free from contact with oil of any kind. Soft rubber articles are often preserved by being kept submerged in water. Such articles would naturally be small in size and contain no exposed fabric or metallic parts. A typical list would be, tubing, catheters, bulbs, stoppers, etc.

The cause of brittleness Ahrens looks for not in the methods of storing but in unsuitable mixings and wrong vulcanization.

Where one is forced to use chemically active fillers, substances should be added to retard oxidation. Using petroleum, benzol, aniline, pyridine, etc., to regain the elasticity of hardened rubber has, in the end, the opposite effect. The softening lasts only as long as the solvent is present; after its disappearance there is hardening again and an acceleration of the degenerating process.

It has been advised that such goods as druggists' sundries be stored in an air-tight receptacle in the bottom of which is placed a vessel containing benzine, which is allowed to evaporate slowly. Kreusler and Bude in *Der Techniker* recommend the dipping of the articles in a paraffin bath, heated to about 212 degrees F. This does not injure the color or the appearance, but is said to enable the goods effectually to resist both light and

atmospheric influences. From its well-known softening effect on india rubber, however, paraffin is likely to be used with considerable care by rubber manufacturers. In the line of mechanical goods, Turner patented a process for treating both hose and tubing with carbolic acid, either during its manufacture or after vulcanization, in order to preserve it. Torrey also saturated duck with carbolic acid before it was made up into hose.

Mowbray's process for preserving rubber in valves: The use of 20 pounds of india rubber, washed and cut fine, in connection with 5 to 10 pounds of naphthalene; digest 24 to 48 hours, at 180 degrees to 230 degrees F. Masticate in a machine heated to 212 degrees F., until it forms a plastic homogeneous compound. If other substances are to be added, treat as follows:

1. Soluble matters (sulphur, antimony, resins, etc.) dissolve in naphthalene, melted or boiling, and add to above naphthalized caoutchouc at temperature of 240 degrees F.

2. Materials insoluble in naphthalene (oxides of lead and zinc, chalk, etc.) deprive of moisture and heat to 212 degrees F. and add to naphthalized caoutchouc.

This compound can be used for soft or hard rubber, according to the proportion of sulphur used. The object is to preserve the elasticity of rubber and prolong its durability.

Trueman's process for preserving india rubber, and fibers that may be used with it, employs the peroxides of manganese and lead and the black oxide of copper, all of which have the property of decomposing ozone in great quantity, and converting it into oxygen. The inventor believes that ozone is the active agent in producing decay, and, by changing it into oxygen, he arrests such decay. In applying these oxides, he mixes them with ozocerite or tar.

Elworthy patented a process for storing rubber goods in a receptacle filled with nitrogen, hydrogen, marsh gas, or carbonic acid gas. This was recommended especially for rubber goods in India.

Benton (American patent) describes the following: A composition for preserving india rubber, consisting of one part turpentine, as much camphor gum as the turpentine will readily dissolve, and one part linseed oil proportioned to the combined part of turpentine and camphor gum.

Truss (English patent) advises: A mixture of 95 parts of soda-ash and 5 parts of commercial carbonate of ammonia is dissolved in hot water and applied to india rubber articles to preserve or restore them.

Zingler's process treats decayed rubber goods by long solution in boiling water containing tartar emetic; mixed afterwards with tannic acid and calcium sulphite.

#### UNITING RUBBER TO METALS.

THE problem often comes to rubber manufacturers to vulcanize rubber or rubber compounds to iron so that they will not part from it under strain. This is done successfully by a number of different formulas. Where the processes are skilfully carried out, the rubber should adhere so firmly to the iron that it will give way anywhere else in the mass, except where its surface is in contact with metal. The usual chemical basis of these processes is the affinity of the sulphur in the rubber mixing for copper deposited on the metal.

For ordinary roll covering the cast-iron roll is rough turned, after which all grease is removed from the surface by washing with naphtha and exposing the roll to open steam for an hour in the vulcanizer. The thoroughly dry, clean roll is then cemented with a hard-curing rubber cement, upon which is applied a layer of hard-rubber composition, followed by a layer of compound curing intermediate in hardness, and this, in turn, by the softer curing main body of rubber.

ATTACHMENT BY MELTING.—The effectual attachment of rubber to iron, applicable in the case of hand-power clothes-wringer rolls, is by the process of cementing by melting. In detail it is accomplished as follows: The metal shaft is brought to dull redness its entire length and is then used to melt or burn out the hole in the previously vulcanized roll, enough to thoroughly smear both hole and iron their entire length with sticky compound. The iron is then quickly quenched in water to a heat below the melting point of the rubber. At this stage the roll is replaced on the shaft and, with a few blows on the shaft on the anvil, jarred down in place. The heat remaining in the shaft is sufficient to cure the roll so firmly to the iron that on cooling it can only be removed by cutting away the rubber. A little

practice is necessary to judge properly the heat of the iron after quenching, that it may not continue melting the interior of the roll and produce a cavity or unattached spot.

**SOLID TIRES TO STEEL RIMS.**—The steel rims for solid motor-truck tires are provided with coarse grooves to add increased surface and protection against side slip of the hard-rubber ply uniting rim and soft rubber. Frequently the rims are electroplated with brass for chemical union with the hard rubber and sometimes the grooves are undercut or dove-tailed in form to add an interlocking grip. The rims are brushed and cleaned with naphtha, cemented with hard-rubber cement and, when thoroughly dried, the hard-rubber ply is forced into contact with the cemented surface with complete exclusion of the air between. The hard-rubber surface is rendered adhesive with cement and the soft-rubber body of the tire applied. Vulcanization in a mold under extremely heavy pressure in a vulcanizer-press renders the attachment of steel and rubber permanent.

The Garrity and Avery patented process is as follows: nitric acid (41 degrees Baumé), 10 gallons; muriatic acid (22 degrees Baumé), 10 gallons; mix and add pure tin, finely divided, 10 pounds. Immerse the iron for 8 seconds, remove and dip into weak solution sulphuric acid, then wipe with a woollen cloth. Then apply with brush, or otherwise, the following compound: rubber cement,  $7\frac{1}{2}$  gallons; litharge, 6 pounds; and sulphur, 3 pounds. Apply vulcanizable rubber compound at once, and vulcanize.

Hall's process: Water, 100 quarts; caustic potash, 10 pounds; cyanide of potash, 2 pounds; sulphate of copper, 2 pounds; sulphate of zinc, 2 pounds. The pickle and bath are made of water and about 10 per cent. sulphuric acid, the tub being lined with brass plate.

Adam's process: A weak solution of sulphate of copper is made—say 2 or 3 ounces of the crystallized salt to the gallon—and this solution may be acidulated with sulphuric acid—say about  $\frac{1}{2}$  gill of strong acid to the gallon. For a fine film for “dipping” articles of iron, steel, or tin, to which the rubber compound is to be applied, if the metal is copper, it should first be coated with tin, nickel, or iron.



The shellac process calls for a cement made of shellac steeped in ten times its weight of concentrated ammonia, the solution being allowed to stand three or four weeks. This solution is painted on the iron, allowed to dry, and the rubber vulcanized upon it.

The Daft patented process consists essentially in heating the rubber in contact with metal containing an alloy of antimony. When the rubber is to be attached to iron or steel the surface is electroplated with copper, zinc and antimony alloy.

#### GAS PROOFING.

BEFORE india rubber reached its present value in the arts, and before coal gas was generally known as an illuminant, Mollerat obtained oil of caoutchouc by distillation and made a fine quality of illuminating gas from it.

Vulcanized india rubber, whether compounded or pure, is permeable by gas. In making flexible gas tubing, therefore, it must be coated or in some way protected in order to make it gas tight. The common way of accomplishing this is to cover the rubber tube with an outer tube made of glue, glycerine, and bi-chromate of potash, this covering being protected in turn by a woven fabric. Another plan for accomplishing the same result is to have an outer and inner tube of india rubber, between the two being vulcanized a sheet of tin-foil.

Pellen rendered india rubber impervious to gas by coating it with collodion mixed with a very small quantity of castor oil or with a varnish composed (1) of 32 per cent. of gum arabic, 8 per cent. of sugar, and 60 per cent. of water, or (2) made from 28 per cent. of dextrin, 60 per cent. of water, and 12 per cent. of gelatine.

Bousfield rendered vulcanized india rubber impermeable to gas by applying linseed oil to it in the form of a varnish, the articles being heated.

GAS PROOFING FOR BALLOONS.—The following mixings are those approved by Churrel for gas balloons:

#### *For Gas-Tight Fabrics.*

Fine hard Para .....	87.00
Paraffin (66 degrees C.) .....	0.75
Sulphur (twice sifted) .....	8.75
Oxide of magnesia (twice sifted) .....	3.50
	<hr/>
	100.00

*For Tensile Strength.*

Fine hard Para .....	54.00
Paraffin wax (66 degrees C.) .....	0.50
Carbonate of magnesia (twice sifted) .....	35.00
Oxide of magnesia (twice sifted) .....	5.00
Fine sulphur .....	5.50
	<hr/>
	100.00

*For Cold Vulcanized Gas-Tight Fabrics.*

Fine hard Para .....	98.75
Paraffin wax (66 degrees C.) .....	1.25
	<hr/>
	100.00

## ACTION OF METALS ON RUBBER.

THE action of various metals on india rubber has always interested rubber manufacturers. In the memoirs and proceedings of the Manchester (England) Literary and Philosophical Society, 1890-91, William Thomson, F.R.C., and Frederick Lewis published an exceedingly interesting paper on this subject. They covered almost all of the metals that are likely in any way to come in contact with rubber surfaces, and proved what has long been acknowledged by rubber manufacturers: that the action of copper is most harmful. The metals that have no action at all on rubber are gold, silver, bismuth, antimony, arsenic, tin, chromium, iron, nickel, cobalt, zinc, and cadmium. Those that act only in a slight degree on rubber are lead, aluminum, palladium, and platinum.

Of the salts of metals that are very destructive, copper stands first, manganese oxides and nitrates of silver being, however, almost as bad. Several other nitrates have also an injurious effect, although not as much so as those just mentioned. They are the nitrates of ammonia, uranium, sodium, and iron.

According to N. Foden, a well-known English expert, proofed goods in browns have caused him more trouble by deterioration than any other colors—more than black, even—and it is to be noted here that blacks as a rule are viewed with distrust by manufacturers, because it is believed generally that copper salts are used in the dyeing. Mr. Foden instances the time when brown tweeds were used largely, and when most manufacturers experienced a great deal of trouble with them, as the browns showed early signs of decay, while the grays remained soft and flexible. Mr. Foden suggests that, as certain dyers use

lime, which is cheaper than logwood, this may act destructively upon the rubber.

Morgan holds that tackiness in crude rubber may be caused by salts of copper. His experiments with rubber latex and copper salts demonstrated that tackiness is produced in proportion to the copper salts present.

Schidrowitz considers that tackiness is due to a physical change in the rubber molecule and not to a change in its chemical composition.

#### SHRINKAGE OF RUBBER.

THE following table shows the average rate of shrinkage in the various leading grades of india rubber, and also the widest range of shrinkage noted in the practice of some extensive manufacturers. The figures express percentages in weight:

Para sorts:	Average	Range
Fine .....	16 to 18	15 to 20
Medium .....	17 to 19	16 to 22
Coarse .....	22 to 28	18 to 35
Mangabeira .....	25 to 30	20 to 35
Caucho .....	26 to 34	20 to 40
Centrals .....	26 to 32	20 to 40
Africans:		
Tongues .....	19 to 24	18 to 25
Flakes .....	28 to 33	25 to 35
Thimbles .....	22 to 28	15 to 35
Accra sorts .....	24 to 32	20 to 40
Congo sorts .....	19 to 24	18 to 35
Benguela, sorts .....	16 to 20	16 to 20
Mozambique sorts .....	17 to 28	10 to 35
Madagascar sorts .....	30 to 40	25 to 55
Assam .....	23 to 31	8 to 45
Borneo .....	33 to 38	30 to 45

Mr. T. Bolas, in his "Cantor lectures" on india rubber, in 1880, gave the following estimates of shrinkage of these leading grades:

Para .....	15 per cent.
Para negroheads .....	25 "
Ceara .....	28 "
Guayaquil .....	40 "
Borneo .....	25 "
African ball .....	25 "
African tongues .....	35 "
African niggers .....	25 "
Madagascar .....	25 "

#### PARA RUBBERS.

The next table indicates in detail the percentage of shrink-

ages in the various grades of Para rubber, also determined by the practice of American manufacturers:

	Fine	Medium	Coarse
Bolivian .....	15 to 17	16 to 18	20 to 25
Mollendo .....	15 to 17	16 to 18	.....
Madeira .....	15 to 18	16 to 19	20 to 25
Manaos .....	16 to 17	17 to 18	18 to 22
Upriver .....	16 to 18	17 to 19	18 to 25
Matto Grosso .....	16 to 18	17 to 19	20 to 28
Angostura .....	16 to 18	17 to 19	25 to 30
Caviana .....	16 to 18	18 to 20	25 to 30
Itaituba .....	17 to 18	18 to 19	20 to 25
Islands .....	18 to 20	18 to 22	25 to 35
Cameta .....	.....	.....	30 to 35

The shrinkage of Mangabeira (Pernambuco) thin sheet is about 25 to 30 per cent.; thick sheet, 30 to 35; ball, 20 to 25. Caucho (Peruvian) slab, 30 to 40; sheet, 30 to 35; strip, 25 to 35; ball, 20 to 25.

The better grades of centrals shrink from 25 to 30 per cent.; other grades, generally from 30 to 40.

#### AFRICANS.

The Gold Coast sorts (including Accra, Cape Coast, Saltpond, Addah, Quittah, and Axim) range about as follows: buttons or biscuit, 20 to 30; flake, 30 to 35; lump, 30 to 40; niggers, 20 to 35.

Cameroon ball, 18 to 25; clusters, 18 to 28.

Lagos buttons, 25 to 35; lump, 30 to 40; strip, 25 to 35.

Congo buttons, 25 to 30; ball No. 1, 20 to 25; ball No. 2, 25 to 35; Upper Congo ball and strips, 20 to 35; red ball, 18 to 22; Equateur small ball, 16 to 20; mixed ball, 18 to 22; Lopori small ball, 16 to 22; Kassai black twist, 18 to 22; red twist, 20 to 25; ball, 20 to 25.

Benguela (and Loanda) sausage, 16 to 20; niggers, 18 to 20.

Mozambique (including Lamu) ball No. 1, 10 to 15; ball No. 2, 15 to 25; ball No. 3, 25 to 35; sausage, 20 to 35.

Madagascar pinky, 30 to 35; Majunga, 30 to 35; black, 30 to 40; niggers, 30 to 40.

#### EAST INDIAN.

Assam No. 1, 10 to 15; No. 2, 20 to 30; No. 3, 30 to 35.

Penang, No. 1, and Java No. 1, 10 to 15 per cent.; other numbers same shrinkage as Assam.

E. Chapel gives this table of percentage of shrinkage:

Para, fine .....	12	Ceara .....	28
Para, coarse .....	25	African ball .....	28
Loando .....	17	Madagascar .....	28
Colombia .....	20	Assam .....	28
Java .....	22	Gaboon .....	35
Gambia .....	24	Borneo .....	35

#### TO FIGURE SHRINKAGE IN CRUDE RUBBER.

It is strange that there should be a divergence of opinion and method in arriving at the net cost of rubber after washing, sheeting, and drying it, yet such is the case. To assist those who have not studied this question, the right and the wrong way of figuring on shrinkage is given here. Take, for instance, an average-priced rubber:

##### *Example A.*

100 lbs. rubber at \$0.50 =	\$50.00
20 lbs. shrinkage = 20 per cent., or 1-5th.	
<hr/>	
80 lbs., net cost \$50.00, as above.	
80 ) 50.00 (	62.50
	48 0
	<hr/>
	200
	160
	<hr/>
	400
	400
	<hr/>

Some persons, however, figure in this way:

##### *Example B.*

100 lbs. at \$0.50 lb.	
Shrinkage 20 per cent. = 1-5th.	
\$0.50 + 1-5th (10 cents) =	60 cents.
<i>Example A.</i> —Correct method—net cost .....	\$62.50
<i>Example B.</i> —Incorrect method—net cost .....	60.00
	<hr/>
Difference .....	\$2.50

This is a difference of 4 per cent., which, if it occurs in manufacturing a large amount of goods where rubber is the greater part of the compound, would make quite a difference in the profit.

#### SPECIFIC GRAVITY OF RUBBER.

THE following records of the specific gravities of different samples of india rubber have been collected:

Best Para, taken in dilute alcohol (Ure).....	0.941567
Best Assam, taken in dilute alcohol (Ure).....	0.942972
Best Singapore, taken in dilute alcohol (Ure).....	0.936650



Specific gravity of rubber (*Continued*):

Best Penang, taken in dilute alcohol (Ure) .....	0.919178
Caoutchouc (Julian) .....	0.920000
Crude caoutchouc of India (Adriani) .....	0.966800
Black caoutchouc (Adriani) .....	0.945200
Prepared from juice in pure state (Faraday) .....	0.925000
Determined by E. Soubeiran .....	0.935500
Determined by Payen .....	0.925000

Faraday's general analysis of the latex of the *Hevea* is:

Caoutchouc .....	30.70
Albuminous extractive and saline matter .....	12.93
Water .....	56.37

The specific gravity of the latex quoted was 1.012.

The crude rubber itself is made up of the following general composition: carbon, 87.5; hydrogen, 12.5.

## PUNCTURE FLUIDS AND TIRE FILLERS.

CAMPBELL'S AND CUSHMAN'S PUNCTURE FLUID.—A mixture consisting of: water, 2 quarts; granulated cork, 4 ounces; powdered cork, 2 ounces; French chalk, 1 pound; white lead, 8 ounces; and gum arabic, 2 ounces. Canadian patent.

CYCO is a popular compound, said to serve as a preserver of tires as well as healer of tire wounds. It is made of vegetable gums that will not harden; neither will it interfere with vulcanizing in the event of a large rupture.

DOW'S INNER TUBE FILLER.—A mixture of paste and feathers held in a continuous pocket that covers the tread of the inner tube.

ELASTES.—An English compound made of glue, glycerine, and chromic salts.

EVERLASTIC is a substitute for air, and by some considered a good compound. As a liquid it is forced into the tire until the desired pressure is reached, and in a comparatively short time it solidifies and is said to become like rubber. It is not affected by heat or cold.

FAGIOLI, under a British patent, produces a composition consisting preferably of these proportions: 1 pint giant cement, 1½ pints of rubber solution, and 2½ gallons granulated cork.

FRANKENBURG'S PUNCTURE FLUID.—Made of dead Borneo, oxidizable vegetable oil, and sulphur; a British patent.

INRIG, under a British patent, prepares a rubber substitute from the gelable portions of animals. Fifty parts of such material are treated with 50 parts of water and from 20 to 60 parts of oil at a temperature of 200 degrees F. Subsequently sodium stannate and potassium bichromate are added. On heating to 212 degrees F. a mass is obtained which may be set in a mold and used for filling motor tires.

NEWMASTIC.—A tire filler, the component parts of which are a secret, but which is apparently of the glue and glycerine type.

PUNCTURE CLOSER.—A British compound: 10 parts gutta-percha, 60 virgin wax, 5 tallow, 20 rosin, 5 wild thyme.

ROLAND'S PUNCTURE COMPOUND.—Glue and glycerine, to which is added sugar or molasses.

RUBBER FOAM OR CELLAZOTE is the invention of an Austrian engineer, Fritz Pfeumer, of Dresden, Saxony. It is being used successfully as a filling for automobile tires in war service under the name of "Cellazote," thus displacing inner tubes. The material consists of pure rubber in a remarkably soft, spongy state. Its manufacture is based upon the observation that rubber as well as gutta-percha and balata are not homogeneous or impenetrable substances, but represent a microscopic reticular structure into which gas can penetrate and remain under certain conditions. Rubber foam can be produced either in the form of soft rubber or in the form of hard rubber.

To make soft rubber foam, rubber is subjected in an autoclave to the high pressure (80 to 300 atmospheres) of an optional gas (nitrogen) and is vulcanized. Under the high pressure the gas penetrates the rubber so that when vulcanization is sufficient and the gas pressure removed the rubber thus treated swells into a foam-like mass, the volume of which is from 13 to 18 times that of the original rubber before treatment. This foam-like mass is made up of a multitude of closed cells, each of which contains, under pressure, a portion of the gas that was forced into the rubber during the vulcanization. The size of these cells and the pressure of the gas they contain can be varied indefinitely by manipulations of the manufacturing process. For making hard-rubber foam the process is continued by placing the

soft-rubber foam in iron retorts and subjecting it to heat and pressure, continuing the vulcanization until the desired degree of hardness is obtained. The shape and conformation may also be equally varied.

It is very light (about 100 pounds per cubic yard of volume), is both gas- and water-proof and affected only by strong acids. The cost of production varies with the price of crude rubber, and is rather higher than the final cost of good soft or hard rubber. One pound of rubber foam has the same volume as 18 pounds of solid rubber.

A variety of practical applications is claimed for rubber foam, due to its bulk and cellular structure. The list includes its use as a substitute for cork in life belts; filling for pneumatic tires and playing balls, imparting resiliency regardless of punctures; insulation of heat and cold in clothing for autoists and aviators and in walls of refrigerators; also for upholstery and other cushioning purposes.

While not affected by acids generally, rubber foam will dissolve in ammonia, which can be used to soften hard foam to facilitate working it. When the ammonia is evaporated hard foam regains its original hardness. It is said to be susceptible of fireproofing.

**RUBBERINE.**—A special solidifying liquid tire filler made in England, very largely used for filling the tires of armored cars, lorries, kitchen cars, and ambulances of the Entente Allies, for service on the battlefields of the Great War. An interesting point is that pneumatic tires returned from the front for refilling, although riddled with shrapnel bullets, had served their purpose until the car got safely back to its base.

**SCOTT'S PUNCTURE FLUID.**—Fifty parts milk, 17 parts isinglass, 200 parts gelatine, 10 parts carnauba wax, 3 parts formaldehyde, 1 part gum ammoniacum. Of British origin.

**SUBER'S FILLER.**—One ounce carnauba wax,  $\frac{1}{2}$  ounce gum tragacanth,  $\frac{1}{2}$  ounce water. Add glue and mix in steam.

**TIRE LIFE.**—A tire filler of the glue and glycerine kind.

## CHAPTER XV.

### SYNTHETIC RUBBER.

THE researches on the chemical constitution of caoutchouc, or rubber, and the sources and processes available for its synthesis, have been outlined by B. D. W. Luff in the "Journal of the Society of Chemical Industry" (October 16, 1916). The author's paper may be summarized as follows:

Between 1835 and 1840 the study of caoutchouc was undertaken on scientific lines by various investigators, including Dalton, Liebig, Himly, A. Bouchardat, and Gregory, but in all cases their work was more or less disjointed. The most systematic attempt to isolate and examine the various products present in the crude distillate from caoutchouc was made by Greville Williams in 1860. He obtained (1) a liquid boiling at 37 degrees C. to which he gave the name "Isoprene"; (2) a large proportion of a hydrocarbon boiling at 170 to 173 degrees C., which was identical with a body previously obtained by Himly, and called caoutchoucine—this has since been proved to be dipentene; (3) a fraction boiling above 300 degrees C., to which he gave the name "Heveene."

Gustave Bouchardat in 1879 undertook a detailed investigation of isoprene, in the course of which he examined the action of hydrochloric acid. He noted that an additional product was formed, but under certain conditions the action of the acid resulted in the formation of a solid mass, not containing chlorine, but having, in fact, the same percentage composition as isoprene itself. He described this body thus: "It possesses the elasticity and other properties of rubber itself. It is insoluble in alcohol, swells in ether and also in carbon bisulphide, in which it dissolves after the fashion of natural rubber." He also noted that on distillation it yielded the same hydrocarbon as in the case of the natural product. This was an important step in the synthesis of caoutchouc; in fact, in order to make this complete, all that was necessary was to prepare isoprene from elementary materials. At that time the only source of isoprene was rubber itself.

Bouchardat's results were confirmed in 1882 by Tilden, who observed the polymerization of isoprene. In discussing isoprene he remarked that one of its chief characteristics was its conversion into true caoutchouc when brought in contact with certain chemical reagents. He pointed out that this was of great practical interest as, if isoprene could be obtained from some other and more accessible source, the synthetical production of rubber could be accomplished. Two years later he succeeded in obtaining isoprene by passing the vapors of turpentine through a hot tube.

The outcome of the work of these two investigators was that the caoutchouc molecule was shown to be formed by the union of a number of molecules of isoprene, and this union or polymerization could be brought about by treating the isoprene with suitable reagents. To them must be given the major share of the credit for laying the foundation of the numerous processes since suggested for preparing synthetic rubber.

In 1887 Wallach observed that isoprene undergoes polymerization on exposure to light with production of a rubber-like mass. In 1892 Tilden showed that the material obtained in this manner could be vulcanized with sulphur. The synthesis of isoprene, and as a corollary, that of caoutchouc, was accomplished by Euler in 1897.

In 1909, owing to the rapid rise in the price of rubber, the problem was taken up in England in a systematic manner by Perkin, Fernbach, Weizmann and Mathews and in Germany by the Bayer and Badische companies. In 1884 Tilden suggested that not only isoprene, but its homologs, should be capable of polymerization in a similar manner. This was found to be the case, and these bodies, chief among them butadiene, form the basis of methods for obtaining synthetic caoutchoucs.

#### PRESENT STATUS OF SYNTHETIC RUBBER PRODUCTION.

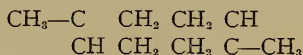
DR. F. W. HINRICHSSEN, in the "*Zeitschrift des Vereines Deutscher Ingenieure*," discusses the present situation in regard to the synthetic production of rubber or caoutchouc. There is not to-day the enthusiastic interest in the matter that existed a few years ago, although it is one of great scientific importance.

Dr. Hinrichsen in his review confines himself to the essen-



tials of the problem, observing that a complete history of its development is impossible, because only a small part of the work done along this line in commercial laboratories has come to the attention of the public.

Harries in 1905 determined the chemical constitution of natural rubber,  $C_{10}H_{16}$ , as that of a 1.5 dimethylcyclo-octane of the formula



In 1909 Dr. Fritz Hofmann and Dr. Carl Coutelle, chemists of the Elberfeld Dye Works, devised a process for absolutely pure isoprene and were the first to convert it into rubber by simply heating it in a closed tube separately or in the presence of certain other substances. A sample of this rubber was sent to Harries, who proved chemically with absolute certainty that it actually was rubber. As the method of Hofmann and Coutelle was not then publicly known, Harries took up experiments to transform isoprene into rubber. In a lecture in Vienna in 1910 he reported his observation that it was possible to convert isoprene into rubber by heating in a closed tube in the presence of glacial acetic acid. Harries deserves credit for thus publishing a method which could be repeated by others.

Creditable work in the technical development of the problem was done by numerous individual German and other scientists, by the Elberfeld Dye Works and by the Baden Aniline & Soda Works. In the original patent specification of the Elberfeld Dye Works the inventors did not confine themselves to the use of isoprene as the basic material, but included the use of a series of hydrocarbons of similar composition and behavior toward polymerization, namely hydrocarbons with a so-called system of conjugated double bonds, such, for example, as erythrene and dimethylbutane and many other similarly constructed substances.

On account of the differences in the basic material there was a possibility of obtaining a series of different rubbers which naturally differed in their chemical constitution. It was also found that the process of polymerization was capable of modifications and that the rubbers obtained by employing different methods with the same basic substance varied among themselves.

It was thus observed independently by Harries and the English investigators, Mathews and Strange, that polymerization in the presence of metallic sodium proceeds at great velocity and the resulting rubber differs materially in its properties from that produced by mere heating. The chemists of the Baden Aniline & Soda Works found that if polymerization by sodium is carried on in an atmosphere of carbonic acid the results are different. A further process worked out by the same company is based on the use of ozonizers on peroxide as catalyzers.

Thus various rubbers may be obtained differing from each other in their properties according to the nature of the prime materials and the method of polymerization. The following compilation, according to Holt, is a concise résumé of a series of such differing rubber-like substances.

#### RUBBERS FROM BUTANES.

STANDARD RUBBER (by heating).—Easily soluble, elastic and capable of being vulcanized.

OZONIDE RUBBER.—Insoluble, strongly inflatable, very elastic, not capable of being vulcanized.

CARBONIC ACID RUBBER.—Not soluble, not inflatable, moderately elastic, not capable of being vulcanized.

SODIUM RUBBER.—Easily soluble, elastic, capable of being vulcanized.

#### RUBBERS FROM ISOPRENE.

STANDARD RUBBER.—Easily soluble, elastic, capable of being vulcanized.

OZONIDE RUBBER.—Soluble only after calendering, strongly inflatable, elastic, capable of being vulcanized.

CARBONIC ACID RUBBER.—Insoluble, not inflatable, elastic, capable of being vulcanized.

SODIUM RUBBER.—Easily soluble, not elastic, can be vulcanized incompletely and only with difficulty.

#### RUBBERS FROM DIMETHYL BUTANES.

STANDARD RUBBER.—Easily soluble, not elastic, capable of being vulcanized as hard rubber only.

OZONIDE RUBBER.—Soluble only after calendering, inflatable, not elastic, can be vulcanized as hard rubber only.

CARBONIC ACID RUBBER.—Insoluble, not inflatable, not elastic, can be vulcanized only with difficulty and is easily oxidized.

SODIUM RUBBER.—Soluble and insoluble modifications, inelastic and incapable of vulcanization.

This possibility of obtaining substances of varying properties by changing the basic materials and the process of polymerization gave rise to the hope of producing at will rubbers with properties adapted to special applications, somewhat as in the dyestuffs industry colors are modified at will. The commercial importance of rubber synthesis depends on the product equaling natural rubber in two respects, price and practical applicability.

The price factor depends in the first instance on the manufacturing cost of the hydrocarbons of the isoprene series which are used as the basic materials.

Progress has been made in this field by the Baden Aniline & Soda Works, which starts with certain fractions of petroleum. Other available substances are starch, amyl alcohol, turpentine, acetylene, etc. With all the processes there are such large quantities of by-products that their removal or utilization would constitute a problem even more difficult than that of the production of the rubber itself. At present there is no possibility of serious competition of artificial with plantation rubber as regards price.

As regards practical utility synthetic rubbers seem to lack the durability of natural rubber because the latter, by its vegetable origin, contains a series of associated substances, resins, albumen, etc., which undoubtedly have an influence on its durability, for it is well known that deresinated rubber is much more easily attacked by the oxygen of the air than rubber containing resin. Possibly these associated substances act as protective colloids which reduce the vulnerability of the pure substance.

A further reason why synthetic rubbers are inferior to natural rubber in mechanical properties is that the former are not uniform substances, but mixtures. According to recent investigations of Steimmig, in the oxygen splitting of synthetic rubbers there appears in addition to coulinic acid and coulinic aldehyde (which, according to Harries, correspond to natural rubber), resinous acid and acetonyl-acetone.

The two last-mentioned substances indicate that in the polymerization of isoprene, in addition to the 1.5-dimethylcyclooc-

taness, a smaller amount (20 per cent.) of the 1.6 compound must have been formed by abnormal condensation, which, upon being split by means of ozone, furnishes the two components mentioned. The latter have never been found in natural rubber. Until possible to arrange the conditions of polymerization so that the synthetic rubbers will constitute uniform compounds, it is not to be expected that synthetic rubbers will equal natural rubber in its useful properties.

Synthetic rubber has been attained as a triumph of chemical science and the researches have been a great contribution to our knowledge. Nevertheless, synthetic rubber is not an industrial success, even in Germany under the stimulus of imperative war needs.

Therefore the following cautions on the subject may still have practical value:

Every year there is more or less newspaper prominence given to synthetic rubber discovery and discoverers, but so far absolutely nothing has been accomplished commercially. The producers of alleged synthetic rubber work along a variety of lines. There is, first and most dangerous, the line of fraud, where real rubber disguised is put forth as a cheap synthetic production. This procedure has been the means of extracting many dollars from the pockets of the credulous. There is another class of honest but somewhat ignorant inventors who make products that in some respects are similar to rubber, and which they believe are equal to or even better than rubber. They use oils, gums, cellulose, in fact, almost anything that will produce a waterproof plastic. These products are often of value in connection with rubber and sometimes when used alone, but never yet have anywhere near equaled the crude material.

## CHAPTER XVI.

### VULCANIZATION WITHOUT SULPHUR.<sup>1</sup>

FROM its inception the world's rubber industry has depended upon sulphur to effect vulcanization. The possible advantages to be derived from a practical method of vulcanization without sulphur are to be found in freedom from "blooming" or "sulphuring up" of the goods, deterioration on aging due to excess of sulphur and the possibility of using as pigments colors not permanent in the presence of sulphur. The Russian chemist, Ivan Ostromislensky, of Petrograd, has conducted extensive researches on vulcanization without sulphur, and is the inventor of a number of processes on the subject. The following pages embrace his publications on the problem:

The hot vulcanization of caoutchouc discovered by Goodyear (1839) proceeds, as is well known, under simple conditions; a homogeneous mixture of caoutchouc and sulphur is heated at 130 to 145 degrees C. As a result, the initial caoutchouc loses its plasticity, and separate pieces of fresh fractures no longer exhibit the power of adhesion. The solubility is lowered, and the "interval of elasticity" increased; the fatal temperature of well vulcanized natural caoutchouc lies at about —35 degrees, that of the chemically pure product being about —18 degrees. What takes place during the heating of the caoutchouc? Attempts to explain this peculiar process have exhausted all the theoretical possibilities. Some investigators regard it as an exclusively physical process, and others as solely a chemical reaction, while many authors consider vulcanization to be determined by both physical and chemical changes.

Since all phenomena, at any rate, of unorganized nature, are divided into only two groups—the physical and the chemical—

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<sup>1</sup> "Mechanism of the Process of Vulcanization of Caoutchoucs," by IVAN OSTROMISLENSKY, in the "Journal of the Russian Physico-Chemical Society," 1915, pages 1,453-1,461. Translated by Thomas H. Pope, B.Sc. Translation revised by Dr. H. P. Stevens, published in the "India Rubber Journal," September 30, 1916.



there can be no essentially new theory of vulcanization. Nevertheless, the nature of the mechanism of the process even yet remains unexplained.

The supporters of Weber's chemical theory regard vulcanized solid caoutchouc (ebonite) as a polymeride of the compound,  $C_{10}H_{16}S_2$  (16 per cent. of sulphur), while others, for instance, Erdmann, consider it to be the thiozonide,  $C_{10}H_{16}S_3$ , or even a dithiozonide. On the other hand, many identify the vulcanization of caoutchouc with the process of "swelling" of colloids or that of gelatinization or adsorption, that is, with the processes of formation of solid or semi-solid solutions.

Some of the supporters of the "mixed" theory consider that the sulphur itself swells or is adsorbed or dissolved in the free caoutchouc, whereas other authors assume the preliminary formation of a compound of the caoutchouc with the sulphur—although only in insignificant amount—this compound being then adsorbed in the still unchanged caoutchouc.

I shall not devote time to the extensive literature of this question, but shall proceed immediately to the conclusions which result from my observations and my new methods for vulcanizing caoutchouc.

Until now no method of vulcanizing caoutchouc has been known in which any organic or mineral compound not containing sulphur is used as vulcanizing agent.<sup>2</sup> But the chemical and especially the physical theories of vulcanization anticipate the possible existence of a whole series of such compounds. I decided to attempt to find substances which may replace sulphur in the vulcanization of caoutchouc.

It was thought that the investigation of the action of homologs and analogs of such substances on caoutchouc and that of the external conditions of the new process—the influence of different admixtures, accelerators, etc.—might elucidate the mechanism of vulcanization itself.

This task has now been completed, and two new methods for the hot vulcanization of caoutchouc have been discovered.

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<sup>2</sup> The process of vulcanization is often termed the sulphuring of caoutchouc. Vulcanization by calcium or sodium hypochlorite or free hypochlorous acid, like vulcanization by hogenes (bromine, iodine, or iodine bromide), leads, as is known, only to "horny" rubber, *i.e.*, to ebonite-like substances. Compare Marckwald and Frank, "Über Herkommen und Chemie des Kautschuks," Dresden, page 62.

When heated with unsaturated hydrocarbons, sulphur produces a twofold effect: it combines at the double bond with formation of thiozonides (Erdmann), or it oxidizes the ethylene grouping, removing hydrogen in the form of hydrogen sulphide, a new ethylenic derivative, or a new compound containing sulphur being thus formed.<sup>3</sup>

On the physical side, sulphur is characterized besides by the ordinary constants (specific gravity, melting point, etc.), and by its ability to exist in different polymorphic modifications (rhom-bic, hexagonal, amorphous, etc.).

In searching for organic substances which vulcanize caoutchouc, like sulphur, the first to be investigated are those which resemble sulphur in oxidizing ethylenes, and at the same time are able to unite at the double linking. Of the physical constants of such substances the essential ones are the melting point and the vapor pressure at the temperature of vulcanization; after these, the solubility in caoutchouc, specific gravity, etc. Besides possessing physical constants near to those of sulphur, the sought-for compounds should exist in polymorphic modifications.

This explains why, in this investigation, I first of all made a halt at compounds containing the nitro-group. These oxidize organic substances (*e.g.*, in Skarup's synthesis of quinoline), and at the same time readily combine with various ethylenes (attention may be called to the compounds of Ar (NO<sub>2</sub>) with polycyclic hydrocarbons and to the author's use of tetranitro-methane as a reagent for double bonds).

1 : 3 : 5-Trinitrobenzene has melting point, 118 degrees C., very near to that of sulphur, *i.e.*, below the temperature of vulcanization, and in specific gravity it also resembles sulphur. Further, most polynitro-compounds exist in polymorphic modifications.

1 : 3 : 5-Trinitrobenzene was the first instance which I hoped would serve as a substitute for sulphur in vulcanization. Experiment completely confirmed my expectation. It was found that both synthetic and natural caoutchoucs are vulcanized more rapidly and easily by various nitro-compounds than by sulphur itself under the same conditions. The result was a product possessing all the associated physical properties of caoutchouc vulcanized by means of sulphur. Experiments were made with both

<sup>3</sup> When acenaphthere is heated with sulphur, the hydrocarbon C<sub>16</sub>H<sub>18</sub> (decacyclene) is formed.

fatty and aromatic nitro-compounds, and vulcanization took place with nitrobenzene, dinitrobenzenes, trinitrobenzenes, tri- and tetra-nitronaphthalenes, picric acid, picramic acid, picryl chloride, "artificial musk," nitro-cyclohexane, and many other compounds.

Further investigation showed that the vulcanizing properties of nitro-compounds do not depend on their capacity for combining at the double linking. As is well known, picric acid combines with ethylenic compounds considerably more readily than most other nitro-compounds of the aromatic series, and yields more stable products. Next in order come picryl chloride, picramic acid, trinitrobenzene, etc.; dinitro- and mononitro-benzenes do not unite at all with ethylenic derivatives.

On the other hand, according to their vulcanizing power, nitro-compounds are arranged in the reverse order, or more accurately, in an order which reveals no analogy between the processes of vulcanization and of combination at the double linking.

Caoutchouc is vulcanized more rapidly and easily by 1 : 3 : 5-trinitrobenzene, after which come dinitrobenzene, mononitrobenzene, tetranitronaphthalene. Picric acid and picryl chloride do not yield satisfactory products; vulcanization undoubtedly begins, but, in spite of many series of experiments, I have never succeeded in bringing it to completion; the caoutchouc partially retains its plasticity, and sticks when fresh fractures are pressed together. Mononitrobenzene, however, gives completely satisfactory results.<sup>4</sup>

The combining capacity of nitro-compounds increases with the number of nitro-groups in the molecule, but we are convinced that the vulcanizing power of nitro-compounds does not depend on this cause. Ostromislensky found that tetranitromethane unites with ethylenic compounds of both the aromatic and aliphatic series, but in no case has it been possible to vulcanize caoutchouc with tetranitromethane, although a large number of attempts have been made.

Various other substances which, like nitro-compounds, are able to unite with ethylenic derivatives, have also been tried,

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<sup>4</sup> Slight adhesion between freshly cut surfaces, as is well known, does not indicate that vulcanization is incomplete, especially with rubber which has been only recently vulcanized.—H. P. S.

among them triphenylmethane and diaminotriphenylmethane. These compounds, in perfect agreement with the above results, cause no trace of vulcanization, the caoutchouc remaining sticky and plastic, and retaining even its pale color.<sup>5</sup> These facts show that the power of nitro-compounds to vulcanize caoutchouc is not determined by their ability to combine with ethylenes.

Is any rôle in the vulcanization played by the capacity of nitro-compounds to oxidize organic substances—by their property of yielding active oxygen with formation of nitroso-compounds? In other words, does the vulcanizing action of nitro-compounds depend on the combination of active oxygen at the double linking of the caoutchouc? This question must, as experiment shows, be undoubtedly answered in the affirmative. First of all, nitroso- and isonitroso-compounds do not vulcanize, as is shown by experiments with nitrosobenzene and isonitroso-camphor under various conditions. This result leads to the assumption that the vulcanizing power of nitro-compounds belongs to one of the oxygen atoms of the  $\text{NO}_2$  radicle. It follows, therefore, that under suitable conditions caoutchouc should be vulcanized by ozone or ozonides, or by various peroxides, peracids, etc.

This fundamental conclusion has been confirmed by direct experiment, a second new method having been found for the hot vulcanization of caoutchouc by compounds containing active oxygen. Special attention has been paid to the vulcanization of natural and synthetic caoutchoucs with benzoyl peroxide and perbenzoic acid. It is found that caoutchouc is vulcanized by benzoyl peroxide incomparably more rapidly and easily than by sulphur or even nitro-compounds.

In order to confirm the deciding part played by the oxygen atom, attempts were made to vulcanize caoutchouc with barium peroxide. This substance yields its oxygen with moderate rapidity only at very high temperatures, and should not effect vulcanization<sup>6</sup> if the latter is determined by the combination of

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<sup>5</sup> This again is not necessarily an indication that vulcanization has not taken place.—H. P. S.

<sup>6</sup> It has been already found that the melting point of vulcanizing substance does not affect the process. Thus, caoutchouc is readily vulcanized by nitrobenzene, which is a liquid, and by tetranitronaphthalene, which melts at 218 degrees, whereas the vulcanization proceeds at 116-145 degrees C.

oxygen at the double linking of the caoutchouc. Actual experiment gives the results expected, since barium peroxide produces no trace of vulcanization.

These new methods of vulcanizing caoutchouc, and the favorable results obtained, are of undoubted scientific and practical interest, and in the first place throw new light on the puzzling mechanism of this process.

We are convinced that the present day vulcanization of caoutchouc begins with a chemical process. Only certain classes of substances—sulphur and some of its derivatives ( $S_2$ ,  $Cl_2$ ,  $Ca S_5$ ), nitro-compounds, peroxides and per-acids—bring about vulcanization. The physical constants and peculiarities of the vulcanizing substances are without influence on the final effect. What can there be common to the physical properties of gaseous oxygen, sulphur, tetranitronaphthalene and perbenzoic acid? At the same time it is sufficient to replace the oxygen of dinitrotriphenylmethane by hydrogen or to remove from the nitro-group of nitro-benzene one atom of oxygen, to obtain a compound—diaminotriphenylmethane, nitrosobenzene—absolutely devoid of the power to vulcanize caoutchouc.

In the process of vulcanization, chemical reactions are allotted, therefore, a definite but still quite modest place. Chemical action with the vulcanizing compound occurs with only a negligible fraction of the initial caoutchouc. Thus, it is found that the complete vulcanization of 100 parts of natural Para caoutchouc requires only 0.5 part of nitrobenzene or 1 : 3 : 5-trinitrobenzene.

There can be no question here of molecular proportions, since 100 parts of  $C_{10} H_{16}$  would correspond with a minimum of 156 parts of  $C_6 H_3 (NO_2)_3$ . Even if it is assumed that  $C_{10} H_{16}$  requires only one atom of active oxygen—which is not true—and that the molecule of trinitrobenzene contains three atoms and that of nitrobenzene one atom of active oxygen, 100 parts of caoutchouc would require 52 parts of trinitrobenzene or 90 of nitrobenzene. Even the corresponding solid ebonite is, however, obtained by vulcanizing rubber in presence of 10-15 per cent. of trinitrobenzene.

Thus, with the actual method for vulcanizing caoutchouc only a vanishing part of the latter enters into chemical reaction,



but this reaction is actually indispensable. The further course of this interesting process is conditioned by physical interaction between the vanishing quantity of caoutchouc which has reacted and that which has remained unchanged.

Thus, we arrive at the conclusion that the vulcanization of caoutchouc is divided sharply into two fundamental phases: (1) A chemical reaction affecting only an insignificant part of the caoutchouc, and (2) adsorption or swelling of the unchanged caoutchouc into the product of this chemical reaction.

Vulcanization may, however, be imagined as an exclusively physical process, since theoretically it may begin with the second phase of the process. Thus, instead of bringing nitro-compound, sulphur, or peroxide into contact with caoutchouc, we may isolate and make use of the minute proportion of substance formed in our first phase; by heating this mixture we should undoubtedly obtain vulcanized caoutchouc. In such case vulcanization takes place in a single phase—adsorption or swelling of the initial caoutchouc into the mixed product, and represents an exclusively physical process typical of caoutchouc. In vulcanization by means of sulphur the existence of the latter in the free state is of no importance, as it is necessary only for the preliminary formation of its compound with caoutchouc, and then only in negligible amount.<sup>7</sup>

The elastic and other properties of caoutchouc vulcanized, for instance, by trinitrobenzene, are qualitatively and quantitatively identical with those of caoutchouc vulcanized with sulphur. Both substances are devoid of plasticity and stickiness and exhibit similar difficult solubility, etc.

Only by chemical analysis might these two vulcanizates be distinguished, although they are obtained by treatment of caoutchouc by absolutely different compounds. The nature of the vulcanizing substances is, therefore, almost without influence on the physical properties, solubility and all the elastic properties of the resulting caoutchouc; it has, further, no effect on the chemical properties of the vulcanizate, since the latter contains only a negligible proportion of foreign substance.

It may again be emphasized that the characteristic changes

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<sup>7</sup> It may be that this compound vulcanizes caoutchouc only when in "*statu nascendi*."

in the properties of caoutchouc produced by vulcanization are determined exclusively by a physical process—the adsorption or “swelling” of the caoutchouc.

These new methods of vulcanization of caoutchouc open up a wide perspective, and it may be that the nitro-compounds, peroxides and per-acids represent only the “first swallow” and that further work will reveal sooner or later other quite diverse substances capable of vulcanizing caoutchouc like sulphur.<sup>8</sup>

Further investigation of this method of vulcanization<sup>9</sup> shows that natural Para caoutchouc is completely vulcanized by as little as 0.5 per cent. of trinitrobenzene, whereas 6 per cent. of sulphur would be required. Further, in the latter case, the unavoidable presence of free, uncombined sulphur lowers the technical value of many rubber wares. The use of different organic compounds for vulcanization of caoutchouc allows of considerable variation in the physical properties, *e. g.*, flexibility, elasticity, etc., besides in the color, smell, etc. Vulcanization may be effected by mono-, di- and tri-nitrobenzenes, -toluenes, etc., tri- and tetra-nitronaphthylamines picramic acid, picryl chloride, artificial musk, nitro-cyclohexane, nitro-dyestuffs, etc. Metallic oxides, which facilitate the vulcanization of rubber by sulphur and enhance the value of the product obtained, exert a similar effect on vulcanization by nitro-derivatives. Lead oxide is most valuable in this respect, and then follow, in order, oxides of zinc, calcium, magnesium, barium. On the other hand, mixtures of aliphatic amines with the above oxides, although they accelerate vulcanization by sulphur or lower the temperature of the process by 10 to 15 degrees C., retard vulcanization by nitro-compounds and lower the value of the corresponding product. Like sulphur and sulphur chloride, nitro-derivatives vulcanize, not only caoutchouc, but also various vegetable oils yielding products analogous to factice.

The vulcanization of caoutchouc by means of peroxides proceeds considerably more rapidly and at a lower temperature than vulcanization by means of sulphur or even nitro-compounds.

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<sup>8</sup> It might be expected on theoretical grounds that caoutchouc would be vulcanized under suitable conditions by oxides of nitrogen, hydrogen peroxide, ozone, ozonides of the terpenes, oxygen or air in presence of compounds which activate oxygen, and many other substances.

<sup>9</sup> From the “Journal of the Russian Physico-Chemical Society,” 1915, pages 1,462-1,467. Abstract from “Journal of Society of Chemical Industry,” Vol. XXXV, p. 59.

The theoretical significance of this process has been already considered in earlier papers.

Vulcanization by the action of benzoyl peroxide has been investigated in detail. It is found: (1) That metallic oxides which accelerate the vulcanization of caoutchouc by means of sulphur or nitro-compounds— $\text{PbO}$ ,  $\text{ZnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ , etc.—are almost without effect on vulcanization by benzoyl peroxide; in some cases they diminish the velocity of the process, and in most instances increase the oxidizability; that is, the rate of decomposition, of the given vulcanizate. (2) Colophony and other resins lower the stability of caoutchouc on vulcanization by benzoyl peroxide. (3) Mixtures of amines and metallic oxides, which were found by the author to act as accelerants of the ordinary vulcanization of caoutchoucs by sulphur, retard vulcanization by the new method and decrease the stability of the corresponding vulcanizate. (4) Proteins exert a similar influence on the vulcanization of caoutchoucs by means of sulphur, nitro-compounds or peroxides; they increase the extensibility and the constant  $K'$ , *i.e.*, the tensile strength of the vulcanizate.<sup>9a</sup>

On normal vulcanization by means of benzoyl peroxide the physical structure of caoutchouc is not destroyed. It is, however, necessary to avoid excess of the peroxide and, for every given benzoyl peroxide mixture, to establish exactly the necessary temperature and time for the vulcanization. If not, the vulcanizate will exhibit, like "abnormal" and also like chemically pure caoutchoucs, negligible extensibility and tensile strength;<sup>10</sup> the protein compounds may be oxidized by the benzoyl peroxide, and their destruction may be accompanied by that of the physical structure of the given caoutchouc.

Caoutchoucs normally vulcanized by benzoyl peroxide exhibit both qualitatively and quantitatively all the typical properties of caoutchoucs vulcanized by either sulphur or nitro-compounds; when kept, they do not change.<sup>11</sup> Caoutchoucs vulcanized with a slight excess of benzoyl peroxide soon (1-5 days)

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<sup>9a</sup> From the "Journal of the Russian Physico-Chemical Society," 1915, pages 1,467-1,471. Translated from the original Russian by T. H. Pope, B.Sc.

<sup>10</sup> Presumably corresponding with over-vulcanization in the case of ordinary rubber and sulphur compounds.—H. P. S.

<sup>11</sup> Samples of vulcanized caoutchouc have been kept for six months without change.

develop on their surface soft, colorless, crystalline leaflets, which are as transparent as glass, and possess pronounced lustre; after the lapse of a longer time (1, 3 or 5 months) the vulcanizate begins to oxidize and gradually becomes sticky; finally it runs, becoming converted into a sticky, more or less viscous, plastic mass.<sup>12</sup> The vulcanizate decomposes especially rapidly when in contact with the original, non-vulcanized mixture, which evidently acts as a "detonator."

Consequently, when different mixtures of caoutchouc and benzoyl peroxide are either heated or stored, two processes take place simultaneously: (1) Vulcanization of the original caoutchouc, this being connected with partial or complete union of the oxygen of the peroxide with the caoutchouc, and (2) oxidation of the caoutchouc by the benzoyl peroxide with formation of the highly sticky mass mentioned above.

The relative rates of these two processes determine the effect of the vulcanization, and experiment shows that these rates depend on the proportion of benzoyl peroxide, on the temperature, and on the prolongation of the vulcanization, and on the nature and quantities of the foreign matters in the initial mixture.

Vulcanization of caoutchouc with benzoyl peroxide requires, therefore, increased attention or skill in the operator.

When once started at a high temperature, the process of vulcanization continues comparatively rapid, even at the ordinary temperature. Thus, it was found that a mixture of normal erythrene caoutchouc and a small excess of benzoyl peroxide converted after 27 days into a very sticky, viscous mass, which later gradually runs or assumes the form of the containing vessel. When previously heated, without access of air, two minutes at 85 degrees C., the same mixture does not run when kept at the ordinary temperature; on the other hand, the stickiness already present disappears spontaneously; the plasticity of fresh sections and their proneness to become sticky are lost, and the mixture gradually vulcanizes at the ordinary temperature, and finally even over-vulcanizes, owing to the excess of benzoyl peroxide present.

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<sup>12</sup> Some caoutchoucs, for instance, normal erythrene caoutchouc, vulcanized with a large amount of benzoyl peroxide, gradually solidify when kept, yielding a dense, brittle mass, easily powdered but absolutely without stickiness.

It is seen that the relative velocity of oxidation, on the one hand, and of vulcanization on the other, depend on the character of the preliminary treatment, in the given case on the two minutes' heating at 85 degrees C.

This fact explains immediately why incomplete vulcanization protects caoutchouc from oxidation or decomposition in the air.

The benzoyl peroxide may be replaced by perbenzoic acid, and probably by ozone, ozonides of caoutchouc or terpenes, nitrogen, oxides, certain metallic peroxides and hydrogen peroxide.

Further, my observations show that barium peroxide produces no trace of vulcanization in caoutchouc. Into natural Para caoutchouc were introduced 1 per cent., 5 per cent., 10 per cent., 15 per cent. and 50 per cent.  $\text{BaO}_2$ , the mixtures being vulcanized for 5 minutes, 10 minutes, 30 minutes, and 2 hours with steam at 2, 3 and 4 atmospheres pressure in a press; under these conditions the mixture underwent no change, its plasticity and even its light color remaining quite unaltered. This interesting observation lends further confirmation to the fact that vulcanization of caoutchouc by the above method takes place at the expense, not of the peroxides themselves, but of their active oxygen.

The accompanying table contains recipes for the vulcanization of different caoutchoucs with benzoyl peroxide. It must be pointed out, however, that the external conditions indicated in this table are by no means ideal.<sup>13</sup>

To conclude, in presence of 0.5-3 per cent. of benzoyl peroxide, normal synthetic caoutchouc, obtained on coagulation of its solution, undergoes at about 80 to 120 degrees C. incomplete vulcanization. The external appearance, and all the new properties of the product obtained, compel the assumption that some forms of natural rubber represent products of incomplete (incipient) vulcanization caused by active oxygen.<sup>14</sup>

Very recently a United States patent [1,242,586] has been granted to Dr. Ostromislensky for a new process of vulcanization and the product resulting. The process is an interesting one, since it eliminates the time-honored use of sulphur for vulcani-

<sup>13</sup> The detailed recipes for the vulcanization of caoutchouc by means of benzoyl peroxide, together with other documents kept in my pocket-book, were unfortunately stolen from me.

<sup>14</sup> Or by compounds containing active oxygen, etc.



zation and may possibly indicate a distinct advance in the development of the industry.

To quote from the patent specification, the process is described essentially as follows:

The invention consists in treating a mass of rubber with halogen or halogen-acid compounds of natural and synthetic rubber, such as rubber chlorides and hydrochlorides, chlorides and bromides of the synthetic rubbers. These substances may be prepared by the direct action of halogens or halogen acids on solutions of rubber. The halogen compound, chloride or bromide of rubber, is first reduced to a fine powder and then combined with the rubber on the mixing rolls. The proportions employed are 10 grams of rubber and 7 grams of 2,3 dimethylethyrene rubber bromide. The material is placed in the vulcanizing press and heated for one and a half hours at 130 degrees C. The product is an ebonite-like mass.

As alternative procedure, 10 grams of rubber, 85 grams of natural rubber bromide heated at 130 degrees C. for two hours, produced a similar ebonite-like material. Seven grams of rubber heated with 10 grams of cauprene bromide at 130 degrees C. for two hours gave a similar result. Three-tenths gram of rubber, heated with 3.6 grams of cauprene chloride at 130 degrees C. for two hours and twenty minutes, gave an ebonite-like mass only superficially colored black.

The substances thus obtained are similar in color to ordinary ebonites, and possess equal stability and physical properties. They do not conduct electricity, may be easily cut and polished and retain the luster even in damp air.

Soft rubber may be produced by vulcanization with hydrochlorides of natural rubber. The preferred proportions given are one part of natural rubber heated with  $16\frac{1}{2}$  parts of hydrochloride of natural rubber at 130 degrees C. for two hours. The resulting soft rubber is generally applicable where soft rubbers produced by sulphur vulcanization have been used.

A similar form of vulcanization takes place when unvulcanized rubber is subjected to the action of an ozonide of rubber.

This ozonide may be prepared by subjecting layers of rubber from one-half to one millimeter in thickness to the action of a stream of dried air under the influence of the rays of a mercury

lamp. After an increase in weight of the original rubber from two-tenths to one per cent. is secured, the product is milled on cold rollers and then reheated for one to 15 minutes at 100 to 120 degrees C. If a small quantity of the ozonides are mixed with unvulcanized rubber and subjected to heat in the usual manner in a vulcanizing press, vulcanization is satisfactorily accomplished. According to the quantity of the ozonides added to the natural rubber, either soft or hard rubber may be produced.

The process is applicable not only to natural rubber, but may be applied to various synthetic rubbers. For example, tests carried out with dimethylerythrene and normal erythrene produced good results.

A British patent [108,300] based on Ostromislensky's researches, has been granted in which vulcanization without the use of sulphur is accomplished by still other groups of agents and accelerators. Quoting from the specifications, the invention is applicable to natural or synthetic rubbers from isoprene, erythrene, and dimethylerythrene. In an example, 50 grams of rubber are mixed with two grams of 1-3-5 trinitro-benzene, one gram of naphthylamine, and ten grams of lead oxide, and the mixture is vulcanized by heating for 55 minutes under a steam pressure of 45 pounds per square inch. The following examples of suitable vulcanizing agents are specified:

Mono-, di-, and tri-nitrobenzols and toluols, tri- and tetra-nitronaphthalenes, picric and picramic acids, picryl chloride, artificial musk, nitrocyclohexane, aurotin, and many other nitro dye-stuffs. Aniline, naphthylamine, pyridine, piperdine and di-isoamylamine are used as accelerators in the presence of metallic oxides; they also prevent aging. Amines may be replaced by traces (0.05 per cent.) of sulphur, antimony, or substances having an alkaline reaction—for example, sodium alcoholate. Oxides of lead, zinc, calcium, magnesium, and barium also act as accelerators. The nitro-compounds and other substances may be employed under all the conditions under which sulphur is employed for vulcanization.

## HOT VULCANIZATION BY NITRO-COMPOUNDS WITHOUT SULPHUR.

Number of Experiment.	Caoutchouc Used.	Grams of Caoutchouc.	Vulcanizing Substance.	Grams of Vulcanizing Substance.	Pbo. Grams of Substance.	Foreign Substances Present.	Pressure of Steam in the Chambers of the Vulcanizing Press.	Prolongation of the Vulcanization in Minutes.	Observations.
1	Para .....	100	1 : 3 : 5-trinitro-benzene.	4	8	.....	45 lbs. ....	45	Vulcanization complete.
2	Para .....	100	1 : 3 : 5-trinitro-benzene.	4	2	.....	45 lbs. ....	45	Somewhat over-vulcanized.
3	Para .....	100	1 : 3 : 5-trinitro-benzene.	4	2	.....	45 lbs. ....	20	Vulcanization incomplete.
4	Crêpe .....	10	Ortho-dinitrobenzene ...	1	3	.....	3 atmos. ....	45	Vulcanization complete; product smells of bitter almonds.
5	Crêpe .....	10	Ortho-dinitrobenzene ....	1	3	.....	3 atmos. ....	60 or 120	Product difficult to distinguish from No. 4.
6	Crêpe .....	100	Ortho-dinitrobenzene ....	16	20	10 grams piperidine preparation No. 2	3 or 4 atmos. ....	5, 10, 45, 120	No Vulcanization.
7	Peruvian .....	10	Nitro-benzene .....	0.5	3	.....	3 atmos. ....	120	Vulcanization complete; possesses smell of bitter almonds.
8	Peruvian .....	10	1 : 2 : 6 : 8-tetranitronaphthalene	1	3	.....	3 atmos. ....	120	Vulcanization complete; the high m.p. 204 degrees C. probably determines the slowness of the process in this case.
9	Crêpe .....	10	1 : 3 : 5-trinitro-benzene.	0.05	3	.....	4 atmos. for 40 minutes and 3 atmos. for 30 minutes.	..	Vulcanization complete.
10	Crêpe .....	10	1 : 3 : 5-trinitro-benzene.	0.08	0	.....	3 atmos. ....	120	30 mins.—vulcanization begins, at 90 mins. becomes apparent, and in 120 mins. is complete.
11	Crêpe .....	100	1 : 3 : 5-trinitro-benzene.	8	0	20 grams MgO.....	3 atmos. ....	45	Vulcanization complete.
12	Crêpe .....	10	β-tetranitronaphthalene..	24	3	.....	3 atmos. for 90 minutes and 4 atmos. for 30 minutes.	..	Vulcanization complete.
13	Crêpe .....	10	β-tetranitronaphthalene..	24	3	.....	3 atmos. ....	150	Vulcanization complete; product possesses an abnormal volume; much greater than the former.
14	Crêpe .....	10	β-tetranitronaphthalene..	1	3	.....	3 atmos. ....	..	Vulcanization complete.
15	Peruvian .....	10	Picramic acid .....	1	3	0.35 gram piperidine	4 atmos. for 30 minutes and 3 atmos. for 30 minutes.	..	Only traces of vulcanization observed.
16	Peruvian .....	10	Picramic acid .....	1	3	.....	4 atmos. for 30 minutes and 3 atmos. for 90 minutes.	40	Almost complete vulcanization, but product not so good as the preceding ones.
17	Peruvian .....	10	Picric acid .....	0.8	3	.....	3 atmos. for 90 minutes.	..	Incomplete vulcanization, product sticky, plasticity partly retained; little elastic and supple.
18	Peruvian .....	10	Picryl chloride .....	0.8	3	.....	3 atmos. ....	30	Product surpasses Nos. 15, 16 and 17.
19	Peruvian .....	10	1 : 3 : 5-trinitro-benzene.	2	0	1.2 grams linseed oil	3 atmos. ....	120	Not vulcanized.
20	Mixture from 19	9.3	1 : 3 : 5-trinitro-benzene.	2	3	1.2 grams linseed oil	3 atmos. ....	45	Vulcanization complete.
21	Peruvian .....	10	1 : 3 : 5-trinitro-benzene.	2	3	.....	3 atmos. ....	60	Physical properties almost identical with No. 20.
22	Peruvian .....	10	0.05 gram 1 : 8 : 5-trinitro-benzene. and 0.05 gram sulphur	..	3	.....	3 atmos. ....	30	Complete vulcanization.
23	Normal erythrene	10	1 : 3 : 5-trinitro-benzene.	0.8	3	1.5 grams colophony.	3 atmos. ....	5	Vulcanization complete.
24	Normal isoprene	8	1 : 3 : 5-trinitro-benzene.	0.8	2.4	.....	3 atmos. ....	5	Vulcanization complete; in 15 mins. (3 atmos.), strongly over-vulcanized product obtained.
25	Abnormal diene-thienylerythrene	100	1 : 3 : 5-trinitro-benzene.	7.5	3	.....	3 atmos. ....	5	Vulcanization complete; elastic point of the vulcanizate lies at about 80-90 degrees C.

## VULCANIZATION BY ORGANIC PEROXIDES.

Number of Experiment.	Caoutchouc Employed.		Caoutchouc.	Grams of Benzoyl Peroxide.	Grams of Lead Oxide.	Grams of Magnesium Oxide.	Grams of Zinc Oxide.	Grams of Foreign Substances.	Pressure of Steam in the Chamber of the Vulcanizing Press.	Time in Minutes Occupied by the Vulcanization.	Observations.
1	Natural Para	.....	20	6 of 30%	..	..	..	..	1 atmos. (119°)	5	Vulcanization complete; product quite transparent; pale cinnamon color.
2	Natural Para	.....	20	4 of 20%	1.5	..	..	..	2 atmos.	15	Vulcanization complete.
3	Mixture of experiment 1	.....	6	..	..	..	..	..	1 atmos.	5	Vulcanization complete; product differs from No. 2 only by its darkish color and its non-transparency.
4	Mixture of experiment 1	.....	..	..	..	..	1.5	..	0.5 atmos.	15	Vulcanization complete; product opaque.
5	Natural Para	.....	5	1 of 20%	..	..	..	..	2 atmos.	15	Vulcanization complete; product opaque.
6	Natural Para	.....	5	1	1.5	..	..	..	2 atmos.	15	Vulcanization complete; product opaque.
7	Natural Para	.....	5	1	..	1.5	..	..	2 atmos.	15	Vulcanization complete; product opaque and tougher and more leathery than Nos. 5 and 6.
8	Dimethylethylene "photopolymeride"	.....	15.6	1.6 of 10%	..	..	..	..	Vulcanized at 80°	15	Almost complete vulcanization; product transparent; at higher temperatures the caoutchouc undergoes profound oxidation. <sup>15</sup>
9	Normal erythrene	.....	6	1.2 of 20%	..	..	..	6 of colophony	1 atmos.	6	Vulcanization complete; over-vulcanized even; product translucent.
10	Natural Para	.....	100	10 of 10%	10	..	..	..	2 atmos.	30	Vulcanization complete; product opaque and possessing sufficient tensile strength. <sup>16</sup>

<sup>15</sup> Products of acid odor are formed, evidently identical with those appearing when this caoutchouc is kept in the air.

<sup>16</sup> When kept, this product does not change in six months.

## CHAPTER XVII.

### RECLAIMED RUBBER AND ITS USES.

THE industry of reclaiming rubber from vulcanized waste-rubber articles developed from experimental beginnings as a necessary adjunct of the manufacture of rubber goods. Reclaimed rubber has risen in estimation and increased in importance, until its output has attained an annual tonnage equaling about half that of the world's total production of crude rubber for the same period. It is thus a very important division of the rubber industry and a marked economic factor in its development. The growth of the rubber-reclaiming trade naturally tends to eliminate the small factory reclaiming plant, because of the more effective economies and the better standardization of product possible under the conditions of operation that obtain with companies of large capital, world-wide connections and specialized effort. Such reclaiming companies employ special machinery, and maintain research and analytic laboratories for control of their processes, standardization of products and study of reclaiming and compounding problems.

Reclaimed rubber, known also as regenerated and devulcanized rubber, can be compounded, manufactured and vulcanized after the manner of crude rubber. The better grades are available as compounding material for quality as well as economy. The lower grades afford inexpensive and useful compounds for many mechanical goods, molded articles and proofed fabrics.

The following figures will give a rough idea of the amount of reclaimed stock produced annually in the United States and the sources from which derived.

Sources	Tons Reclaimed Rubber
Boots and shoes .....	40,000
Automobile tires .....	40,000
Mechanicals and sundries .....	10,000
Inner tubes .....	4,000
Solid truck tires .....	7,000
Total United States production .....	101,000



The vast and varied collections of vulcanized waste rubber are subject to sorting and classification into a number of more or less standard grades before shipment to the reclaimers, who continue the sorting for their own purposes. The official market specifications of waste rubber, standardized by The Rubber Reclaimers Division of The Rubber Association of America, include 34 grades, classified as follows:

Rubber boots and shoes, 5 grades;

Auto tires, 8 grades;

Solid tires, 2 grades;

Hose, 4 grades;

Inner tubes, 7 grades;

White rubber, 3 grades;

Wringer rolls, 2 grades;

Red rubber, 3 grades;

Mixed black rubber;

Matting and packing.

Reclaimed rubber, known also as recovered or regenerated rubber, shoddy, and crumb, is produced from worn-out rubber goods. There are two general methods in vogue, known respectively as the mechanical and the chemical processes. Where the mechanical process is followed, the waste is ground to a fine powder, which is run over magnets to extract the iron, and is then put through a blowing process, which separates the woolen or cotton fibers from the rubber. The rubber powder is then subjected to a high degree of heat (the process known as devulcanization), and afterwards sheeted, when it is similar to unvulcanized rubber compound.

The chemical process is similar to the mechanical, except that the fiber is destroyed by means of acid or alkaline solutions and quite a percentage of it is washed out with the residue after the process is finished. Special grades of reclaimed rubber are made from mechanical goods that have high-grade frictions in them and also from unvulcanized scrap. Rubber is also reclaimed from ordinary mechanical goods such as hose, belting, and packing, and for certain purposes is mixed with what is known as shoe shoddy. White scrap, from wringer rolls, tubing, druggists' sundries, pneumatic tire treads, and the like, is also produced. The great trouble with the white is that, on second vulcanization,

it is apt to be very hard. At one time hard-rubber dust was to be found in the market and was used as a shoddy in certain grades of vulcanite. There is today but very little of it to be found, however, as most of the manufacturers of hard-rubber goods find a use for all that they make.

The processes followed in the reclaiming of waste rubber are no longer secret. Those who are in the business of manufacturing for the trade are able to do it, as a rule, because they buy waste stock at a lower figure than a small user could, besides which, by manufacturing the goods in larger quantities, they can do it more economically and maintain higher average grades than it could be done in a small way.

In this business are used crackers, sheeting mills like ordinary grinders, and, indeed, general machinery not dissimilar to that used in a mill where crude rubber is compounded. They have in addition, however, lead-lined tanks for acid treatment, vulcanizers or, better, devulcanizers, huge vats for washing, magnets for removing metal, sieves, and drying facilities. This branch of the rubber business is not supposed to be deeply interested in compounding, in spite of the fact that it is sometimes suggested that earthy matters, heavy adulterants, and oils do find a use in reclaiming mills.

Rubber scrap of any sort vulcanized or unvulcanized, is actively sought for reclaiming the world over. The larger factories use their own scrap of both kinds yet much unvulcanized scrap gets upon the market chiefly in the form of Para cable strippings, mackintosh cloth cuttings, frictioned fabric, and cement ball.

Next to this in value, and indeed often more valuable, is the pure gum vulcanized scrap, such as rubber thread, and a variety of floating stocks that do not contain rubber substitutes. Special high-grade stocks, such as inner tubes, billiard cushions, balloon fabrics, etc., are favorites in this line.

Automobile tires constitute the largest single item in scrap collection. Ten years ago old rubber boots and shoes occupied this position, and now rank second. Old rubber boots and shoes are graded roughly by the country of their origin—American, English, German, Russian and so on—and their conversion into

workable rubber has long been the backbone of the reclaiming business.

Most of the products of the mechanical goods factory come into the market as waste eventually, and are sorted and graded according to the richness of the compound, and the freedom from metal and fabric. In this line is the red scrap, such as valves; the drab, embracing wringer rolls, mattings, buffers and hose, graded as air brake, fire-hose linings and garden hose. Then there is the grading of belting, asbestos scrap, red and other packing.

In tires there is the collection and sorting of solid tires into cab, baby carriage and truck tires. In pneumatics, there are single and double tube bicycle tires, motor-cycle casing and automobile tire shoes—American, French, and German. There is also the inner tube in gray, red, and black that is today a large factor in the recovery business.

In druggists' sundries, water bottles and the like furnish white and red rubber, while air and water beds, sponges and many other specialties furnish regular grades.

In hard rubber, cells, telephone receivers, sheets and rods are ground up and used again, while hard-rubber shavings and dust find a ready market.

Gutta-percha, in the form of cable strippings, balls and buckets, is a type of waste with a recognized place.

And these are but a few of the many grades put out by the sorters, and sold to the scores of reclaiming plants the world over, that produce tons of usable rubber from what was once thrown away or burned under the factory boilers.

Almost the first attempt at recovering rubber waste was that done at the Beverly Rubber Works, in Massachusetts, back in the fifties, when Hiram L. Hall boiled waste vulcanized rubber in water, after reducing it to a powder, and then sheeted it. It is a curious fact that, in one little mill to-day, the manufacturer grinds his own scrap, boils it in hot water until it is in condition to sheet, and makes a fair article out of it.

The year after Hall's patent, another was granted to Francis Baschnagel, who paved the way for devulcanization by covering a process whereby a finely ground rubber was exposed to the action of live steam. It was not, however, until E. H. Clapp took hold of the business and discovered a process for blowing

the fiber out of the finely ground rubber prior to its devulcanization that the goods began to be used to a large extent.

The next step in the progress of the art was characterized by the taking out of a great variety of patents, most of which depend upon various acids and alkalies for destroying the fiber. These patents were more than fifty in number, and were fully reviewed with their attendant processes in the famous suits brought by the Chemical Rubber Co. against The Goodyear's Metallic Rubber Shoe Co. and the Raymond Rubber Co. While it would be tedious to go into that matter, it is interesting to touch upon important processes involved. The action of acids upon fibers, of course, had long been known; in connection with the rubber business, however, it was without doubt novel. The Hayward patent, for instance, mixed 75 pounds of sulphuric acid with 8 hogsheads of water, and in this way the fiber was weakened so that it was easily ground up with the rubber. The Faure patent called simply for the immersion of the clippings in an acid, which in disintegrating the textile matter set the india rubber free. Hiram Hall advised the use of lime or alum to eat up the cloth, and also a solution of 1 part of sulphuric acid to 9 parts of water. Burghardt used muriatic acid for destroying the cloth fiber. The Heinzerling patent called for a treatment first with acids, and then with alkalies. It is also to be remembered that Charles Goodyear directed that crude india rubber should be subjected to a 10 per cent. solution of sulphuric acid to eat up the bark with which the gum might be contaminated.

The Mitchell patents, the Bourn patents, and others, where an extremely dilute acid was used, and where a concentrated acid was called for, have been so thoroughly reviewed that those familiar with the rubber business know all about the processes employed.

What is known as the alkali process, based upon the patents of Arthur Hudson Marks, is one of the notable improvements in reclaimed rubber in more recent years. Factories for reclaiming under this process are operated in the United States, England, Germany and Belgium, mechanical waste being chiefly used.

In addition to the processes in more general use, a few unusual ones may be interesting. For example, the Torstrick process, in which dilute nitric acid and fusel oil were mixed with

the gum in a heated state, or passed through it in the shape of vapors, making the mass sticky, after which a small quantity of chloride of calcium was added and the gum sheeted.

Conrad Poppenhusen mixed rubber scrap with essential oils, a little turpentine being used preferably, left the scrap until it had become soft, and then passed dry gaseous ammonia into the mass, forming a gelatinous viscid product.

C. F. E. Simond mixed 2 parts of chloride of lime with 100 parts of waste rubber, and brought it to a high degree of heat, by which the sulphur was volatilized, which took from 15 to 60 minutes, and then used the rubber over.

Thomas J. Mayall mixed vegetable tar with waste rubber—exposed it to the heat of the sun, or to a gentle artificial heat, and got a soft pasty mass that he was able to work with crude rubber. He also invented a process for sprinkling the finely ground rubber with camphene and setting the mass afire in a partially covered vessel, his claim being that if the fire was stopped at a certain point, a tough viscid mass was the result, which contained neither sulphur nor fiber, and could be reworked like unvulcanized rubber.

Beylikgy exposed vulcanized rubber for a number of days to a temperature of 250 degrees F., after which he claimed that it became an adhesive mass, insoluble in alcohol, partially soluble in ether, and wholly soluble in benzol. He called this caoutchoucite and claimed that it could be vulcanized with the addition of sulphur at a lower temperature than ordinary crude rubber.

McCartney, of Glasgow, mixed vulcanized rubber with naphtha and a little acetic acid. He also added camphor, and by the action of heat produced in reality a rubber paint.

The following are briefs of some of the later claims of inventors in rubber vulcanizing:

Anderson's process (English). Ground scrap is mixed with calcium sulphide and coal-tar naphtha, exposed to heat, and thoroughly washed.

Alexander's process relates to the production of india rubber latex from rubber waste. The waste is heated under pressure in benzene. The dissolved matter is then removed, and the solution is heated again in sodium hydrate. The benzene is distilled off and the aqueous solution of caoutchouc filtered and precipitated with acid.



Basle process. A Swiss process which covers the use of various ethers boiling at a temperature of about 100 degrees C.

Brimmer's process (German) consists of mixing ground scrap with castor oil, heating until dissolved, adding alcohol for precipitation and washing with a weak solution of caustic soda.

Clift's process (English). Waste rubber is dissolved in a base of the pyridin group, treated with acid in the presence of a volatile solvent for the separation of the rubber from the base, then the solvent separated, leaving with the rubber in solution.

The Chautard process (French) uses commercial phenol for reclaiming, the phenol being later distilled off. The whole process is quite intricate.

The Durvez process (Belgian). Rubber waste boiled with water and finely powdered lime. Product is washed, rolled, and dried.

Eves's process (American). Devulcanizing by treating with sodium sulphate in the presence of heat, then incorporating barium chloride.

French process. Waste vulcanized rubber is heated with terpin hydrate, the mixture is then treated with boiling water, and from the residue the regenerated caoutchouc is extracted by means of a suitable solvent, such as commercial xylol. The terpin hydrate is recovered for use over again by cooling the hot aqueous wash-liquors.

French process. The finely divided rubber is heated, preferably at 110 degrees to 180 degrees C., under pressure, with a soap solution, to which may be added other substances, such as aliphatic or aromatic hydrocarbons, oil of turpentine or the like, and salts capable of forming solutions which dissolve sulphur, such as alkali sulphides, alkali sulphites, etc.

Gilbert-Besaw process (American). This process is not patented, but is secret. It is applicable to the recovery of any sort of rubber scrap, whether cured in open steam, in molds, or in dry heat. According to the statement of the inventors, no acid or alkali, or anything that can be in any way injurious, is added. The machinery for treating the waste rubber for the removal of fiber and for devulcanization is individual to the process. The time occupied in devulcanization is about one-quarter that used

in existing processes. No residuum or oily matter of any sort is added to the product, either before or after devulcanization.

Gregory and Thom's process (English). Reclaimed in the usual way; then a solvent is added which is a mixture of aniline oil and naphtha. The product is heated in open steam until the solution of rubber is complete, when it is taken out and strained.

Gubbin's process (English). Unvulcanized scrap in which the fabric is saturated with naphtha and passed through plain pressure rolls to remove the rubber from the fabric.

Heinzerling's process (German). Ground waste rubber treated with aniline or its homologs at 140 degrees to 180 degrees C. The rubber is then mechanically separated from the residue; is treated with dilute sulphuric acid, and the separating rubber is washed and dried.

Heyl-Dia's process. Heats ground rubber under moderate pressure in naphtha, temperature being not more than 120 degrees F. The naphtha is then drawn off and with it most of the sulphur. The rubber is then heated to over 350 degrees F., with a fresh solvent when it dissolves. The solvent is then removed and the sulphur washed and dried.

Hyatt and Penn's process. Waste rubber finely ground, is put into a vacuum chamber and molded into goods under heat.

Karavodine's process (French) consists of pulverizing the material, adding asbestos fibers which have been previously treated with a binding medium, and subjecting the mass to a higher pressure at higher temperature.

Kessler's process. Waste rubber is treated with carbolic acid in a vacuum. After solution powdered acetate of lead is added and the whole submitted to distillation. Caustic soda is used later for neutralizing.

Kittel's compound (Austrian). Powdered waste mixed with caustic alkalies is compressed into cakes and heated 2 or 3 hours at 280 degrees C.

Koneman's process (American). Ground waste is boiled in a salted-acid solution, and a mixable fixed hydrocarbon is then added.

Koener's process (German). Waste rubber is heated with solvents, such as benzine, for a time, after which the solution is further heated with water and solvent subsequently distilled off.

Marks's process (American). Waste rubber finely ground is heated in a dilute alkaline solution in a closed vessel for a time and at a temperature dependent upon the amount of sulphur present.

Murphy's process (American) uses for devulcanizing a bath consisting of carbonate of soda and gallic acid.

Neilson's process (German). The inventor uses resin oil as a solvent, filters and precipitates the rubber by means of a ketone.

Passmore's process dissolves vulcanized waste with eucalyptol and removes mineral matter by filtrating. The eucalyptol is driven off by having steam forced through the mass.

Penther's process (German). A devulcanizing machine of German origin makes what is known as American reclaimed rubber. It separates the fiber from the rubber so thoroughly that the fluff is a merchantable product in the felt trade.

Peterson's process (American) consists in subjecting shredded waste to an alkaline solution raised to a boiling temperature under hydraulic pressure, next washing in water solution containing phenol under a high temperature and pressure.

Price's process (American) uses caustic solutions of marked strength, under ordinary atmospheric pressure.

Price's process (English). A process whereby waste rubber cut into pieces of suitable size is roughly mixed with crude rubber and ground flint, and without being vulcanized, by great pressure molded into finished goods.

Roux process (French). The inventor describes a machine which devulcanizes powdered waste rubber and makes it into tubing at the same time. In other words it is a combination of a devulcanizer and tubing machine.

Steenstrup's process. The waste is heated in a solution of alkali and hydrofluoric acid under steam. The product is then washed, dried, etc.

Theilgaard's process (Denmark). The inventor has several patents which cover the treatment of vulcanized scrap by alkaline earths and such solvents as sodium sulphide.

Wheeler's process (American) consists in subjecting the waste particles individually to a current of heated fluid moving through a confined passage.

Zuhl's process (English). Vulcanized waste is dissolved in five times its weight of naphthalene at a low temperature. The naphthalene is then distilled from the mixture with steam.

Actual restoration of the rubber content of vulcanized rubber to its original unvulcanized state has not been accomplished by any of the preceding methods. The alkali processes of reclaiming remove the free sulphur, but the product contains all the combined sulphur originally united with the crude rubber. The nature of the problem is purely chemical and the subject of active research.

One of the latest and chemically successful processes is that of Dr. David Spence, from whose patent specifications are quoted the following observations on the chemical nature of the important problem of rubber-reclaiming methods.

The removal of free sulphur from vulcanized rubber can readily be effected and, in conjunction with a certain plasticising or depolymerizing action on the rubber, analogous to the plasticising action of mechanical working and heat on raw rubber, the removal of free sulphur is all that is effected by present-day processes of rubber regeneration. An interesting process described by Spence has for its object the removal of not merely traces of the combined sulphur, but of large proportions of the combined sulphur of vulcanization, and is applicable not merely to rubber waste containing 2 to 3 per cent. of combined sulphur, but to the product of complete saturation of the rubber hydrocarbon, known as hard rubber (which contains as its principal constituent a body considered to have the formula  $C_{10} H_{16} S_2$ ), which may contain as much as 32 per cent. of combined sulphur. The process is in line with the fact that the vulcanization of rubber by sulphur is a reaction whose velocity can be accelerated, and to be technically successful, therefore, requires an accelerator to facilitate the reaction. The more powerful the accelerator employed, the more violent and the more complete will be the reaction. Without such an accelerator the vulcanization of rubber proceeds very slowly, even at high temperatures, whereas in the presence of even a trace ( $1/100$  of 1 per cent.) of a suitable accelerator, vulcanization of rubber by sulphur can be effected in a few minutes. By reason of the character of the vulcanization process it appeared to Spence, therefore, that the

true solution of the problem of effecting a real devulcanization of vulcanized rubber must lie in the use of a powerful vulcanizing accelerator in conjunction with an element capable of combining with and fixing the sulphur liberated from the rubber by the accelerator. The more powerful the accelerator, the more marked should be the results obtained by the means of it, and this principle should govern the choice of the accelerator employed. Theoretically, all that is necessary is a powerful accelerator and an element of substance to combine with the sulphur set free by the accelerator. The presence of this latter substance even will be unnecessary if the accelerator itself is employed in excess and is capable of forming a stable derivative with the sulphur under the temperature and other conditions of the experiment. The principle has been tested by experiments, and it has been found to form the basis of a successful desulphurization of vulcanized rubber, Spence having succeeded in effecting the removal of large proportions of the combined sulphur from vulcanized india rubber by the use of several of the most powerful of those reagents, which are known as "catalysts," or more usually "accelerators," employed in vulcanization. A solution of aniline-potassium or of aniline-sodium in excess of aniline which is formed by the action of dry aniline on metallic potassium, or sodium can be used very effectively in removing combined sulphur from vulcanized rubber; this solution in addition to its accelerant action actually serves as a means of fixing the sulphur liberated from the rubber as an insoluble metallic sulphide. As an example of a powerful organic accelerator, which is very effective in removing combined sulphur, piperidine may be mentioned. Caustic soda—long since shown to be one of the most powerful of inorganic catalysts—is another suitable substance for effecting removal of combined sulphur of vulcanized india rubber. This substance has the advantage of being cheap.

Generally speaking, Spence has found that it is best to work with all components of the reaction in solution; and in this connection the use of a solution of aniline-potassium in excess of aniline sufficient to dissolve the rubber at the operating temperature is particularly advantageous. In this case, the rubber, as well as the accelerator, is brought into intimate contact in aniline solution, and the sulphur which is liberated is thrown out



of the field of reaction as an insoluble alkaline sulphide. In the case where caustic soda is employed as the devulcanizing agent, the less complete devulcanization effected is explained by the fact that no solvent or means has yet been found of bringing this accelerator and the rubber together in homogeneous solution. Vigorous agitation facilitates the reaction. Similarly, the process, in order to effect the best results, should be carried out in absence of moisture, the presence of water having been found to be particularly disadvantageous. The temperature at which the reaction may be carried out may vary within wide limits according to the reagents used; the higher the temperature, within certain limits, the better will be the results obtained, and for practical purposes it is found that a temperature of about 170 to 180 degrees C. is usually advantageous.

As examples of the effectiveness of his process, Spence cites examples of the reduction of the combined sulphur from 78 to 90 per cent. in one operation in soft vulcanized rubber and 73 per cent. in hard rubber.

## CHAPTER XVIII.

### PHYSICAL TESTS AND ANALYSES OF CRUDE AND VULCANIZED RUBBER. SPECIFIC GRAVITY. SPECIFICATIONS FOR TESTING RUBBER GOODS.

It long has been the boast of expert rubber superintendents and manufacturers that they find little trouble in matching compounds. As a matter of fact, some of them are remarkably expert. Given a small sample of vulcanized rubber in a familiar line and the price at which it must be produced, they are often able, without much experimenting, by their knowledge of rubber and compounding ingredients, to get a result apparently similar.

This, in fact, was the only way possible when rubber manufacturers operated on individual knowledge and experience and in self-defense conducted their processes secretly and without scientific assistance. Under modern conditions it is no longer advisable, even for experienced superintendents, to attempt close duplication of particular rubber compositions or to meet specified requirements by inspection for odor, color, weight or qualitative hand tests of strength, stretch and hardness.

Rubber manufacturers are no longer credited by important customers with exact knowledge of what will best serve the needs of the latter; hence specific specifications, the laboratory, the development department, and the introduction of team-work in the coördination of science and practical experience on the part of chemist, superintendent, and heads of factory departments.

To meet these conditions, the rubber manufacturer requires intimate knowledge concerning the origin and preparation of market grades of crude rubber and methods for determining their quality.

Standardization of regular factory product, including considerations of quality as well as price, calls for application of the scientific method.

The production of goods for the army and navy, fire departments and railroads, insulation for power, light and telephone companies and other public or semi-public service cannot be conducted without laboratory facilities in charge of a scientific staff.

The function of a rubber-work's laboratory briefly outlined includes: (1) systematic examination of the chemical and physical characteristics of crude rubbers, compounding ingredients, and accessory materials, such as fabrics and metals used in rubber goods; (2) standardization of materials, compounds, vulcanization and other processes and manufacture of goods to specification; and (3) control of factory processes.

The rubber work's laboratory is usually equipped in close adjustment to the needs of factory control; it therefore varies somewhat, due to the nature of the factory production. In addition to facilities for analytic work it generally includes testing apparatus of general or special adaptability for mechanical and electrical testing. A selection of laboratory-size machinery is very desirable for manufacturing operations on an experimenting scale, such as washing, drying, mixing, calendering, and vulcanizing. The best equipped works' laboratories are essentially rubber factories in miniature, in which complete studies can be made of materials and processes without interference with factory routine or production.

It is unnecessary to mention here the equipment of chemicals and apparatus needed in a laboratory for chemical analysis. Such information is easily accessible in the chemical and apparatus catalogs of laboratory supply houses. The following chemical methods are given in detail because they are standard and issued by the Government and by important official and trade associations.

#### VALUATION TESTS OF CRUDE RUBBER.

SCIENTIFIC and rule-of-thumb valuing of plantation rubber have recently been compared for the Dutch Rubber Congress.<sup>1</sup>

The investigation included 137 specimens, 36 samples of sheet, all but one of which was smoked, and 101 samples of crêpe, six of which were thick blankets. These were all judged

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<sup>1</sup>J. G. Fol, "Mededeelingen van dem Rijksvoorlichtingsdienst ten behoeve van den Rubberhandel en de Rubbernijverheid te Delft."

in an empiric way by the producers and their conclusions reserved and compared after completion of the scientific tests made without knowledge of the first results.

AN ABSTRACT OF THE SCIENTIFIC METHOD AND FOL'S CONCLUSIONS.

Empiric judging of rubber depends largely on color, smell, and stretch. These tests at best are only roughly approximate, although the rubber expert by means of them can distinguish marked differences in quality. It is a mistake to presuppose that mechanical properties of the rubber when vulcanized run parallel to color, smell and stretch in the raw state. Variations in physical condition do not permit hand-pulled tests nor quantitative expression of value. The influence of temperature variations is also marked.

Smoked sheet cannot be judged better by rule of thumb than crêpe. Its color denotes only the degree of smoking. Sheet is easier judged as to its mechanical properties than crêpe.

Black rubber presents the most difficulties for empiric judgment, as it cannot be subjected to a hand test.

Scientific methods obviate these objections, because each sample is suitably prepared and tested quantitatively. The 137 samples under investigation were examined after the following scheme:

A. Chemical Analysis:

1. Moisture.
2. Resin.
3. Ash.
4. Nitrogen calculated as albumen.
5. Rubber.
6. Acetic degree.

B. Viscosity Number.

C. Vulcanization and Physical Tests:

1. Tensile strength.
2. Elongation.
3. Permanent set after 24 hours at 400 per cent. stretch measured after six hours' rest.
4. Temporary set measured directly after release from 400 per cent. stretch.
5. Determination of load necessary to stretch sample 400 per cent. (kilograms per square centimeter).

C. Vulcanization and Physical Tests (*Continued*):

6. Difference of the load necessary to stretch sample 400 per cent. and that required for the last of five successive 400 per cent. stretchings.
7. Elasticity or rebound.
8. Coefficient of vulcanization.

Concerning the importance and correlation of these determinations, Fol concludes: (1) chemical analysis is not sufficient alone for judgment of the rubber quality. Properties of rubber are chiefly determined by the physical nature of rubber and the rubber molecule. The quantitative chemical differences are not enough to account for the large differences found in the physical properties; (2) in general a high viscosity indicates good mechanical properties of the rubber after vulcanization. However, the opposite must be assumed with some reservation, since in studying the relation between the viscosity and tensile strength it appeared that various samples with a low viscosity had a very high tensile strength. The samples that exhibited this relation were almost exclusively smoked sheet. This phenomenon is caused by the fact that it is very difficult to dissolve smoked sheet in benzol completely. The dissolved part has a low viscosity and presumably contributes little to the excellent qualities shown by the sample after vulcanization, while the very considerable amount of undissolved rubber apparently is the most valuable part of the sample and most probably causes the good properties after vulcanization.

The tensile strength permanent set after stretching 400 per cent. and the coefficient of vulcanization were taken as quantities suitable for classifying the samples. These quantities are closely related. Thus, high tensile strength generally accompanies high coefficient of vulcanization and low permanent set. Elongation at break also indicates the quality of the rubber; of samples equally loaded, that is the best which has the highest elongation at break.

The remainder of the physical tests made were set aside as practically valueless for the end in view.

One of the most important points demonstrated by this investigation is the lack of uniformity in first latex rubber. The greatest divergencies were found in viscosity, tensile strength,



permanent set and the coefficient of vulcanization. The causes of this lack of uniformity and its prevention are among the most important problems of the rubber industry.

The rubbers investigated were classified as follows:

Class	Breaking strain (kilograms per sq. c. m.)	Permanent set.	Coefficient of vulcanization.
I .....	135 k. g. and over	Maximum 5%	Minimum 5
II .....	120 k. g. to 135 k. g.	5% to 7%	Minimum 4
III .....	90 k. g. to 120 k. g.	7% to 12%	Minimum 3
IV .....	80 k. g. to 90 k. g.	Over 12%	Below 3
V .....	Below 80 k. g.	Over 12%	Below 3

The division of the 137 samples among the different classes is indicated below:

Class	Sheet	Crepe	Blanket.
I .....	17 <sup>2</sup>	3	0
II .....	12	21	3
III .....	7	51	2
IV .....	0	11	1
V .....	0	9	0
Totals .....	36	95	6

These figures demonstrate clearly that, in general, smoked sheet is better than crêpe. However, there are samples of crêpe that are equal to smoked sheet as far as mechanical properties are concerned. The number of samples of blanket is too small to permit a decisive conclusion, but the figures would indicate that blanket is inferior in quality to smoked sheet and often also to crêpe.

Lack of uniformity in plantation rubber reveals itself chiefly in the difference in rapidity of vulcanization. Two rubbers outwardly of absolutely equal value may produce entirely different results after vulcanization. Empiric judgment cannot tell how a rubber will behave during vulcanization, hence the estimate of value is liable to be incorrect. This causes much uncertainty and disappointment to the manufacturer.

The researches of K. Gorter on the viscosity index as a standard for the preliminary testing of crude rubber are abstracted as follows:<sup>3</sup>

The viscosity index is the logarithm of the viscosity of a 1 per cent. solution and is superior as a standard to the viscos-

<sup>2</sup> One sample unsmoked.

<sup>3</sup> "Chemical Abstracts," October 10, 1916.

ity, being less dependent on the temperature than the latter, 1 degree causing a variation in the viscosity index of only 0.005. Hence it is not necessary in viscosity determinations to keep the temperature constant by means of a thermostat. The viscosity index multiplied by the factor 70 gives the tensile strength of the rubber sample. Gorter's viscosimeter consists of a pipette with a 10 cm. capillary stem with an opening 1.42 mm. in diameter, the whole fitting into a 150 cc. Erlenmeyer. The indicated capacity of the pipette is 15 cc., and its constant 9.8 at 26 degrees C. One gram of rubber is dissolved in 120 c.c. benzene (not purified from thiophene) with shaking, using a brown flask. The solution is filtered after 24 hours and the concentration determined, after which the viscosity is determined by the pipette. The relative viscosity of a rubber solution equals the period of delivery, divided by the constant of the viscosimeter for the solvent used. The viscosity of a rubber solution is dependent on the dimensions of the viscosimeter used; hence to obtain comparable results the same instrument must invariably be used.

Below is outlined Schidrowitz's method for the examination of crude rubber.<sup>4</sup>

The examination of crude rubber may involve:

(a) Chemical analysis, with a view to determining the quantity of pure rubber and of various impurities, and, to a certain extent, in some instances, the nature of the latter.

(b) Physical or mechanical tests, carried out either on the crude material or on the latter modified by the vulcanizing process, with a view to determining the physical and mechanical qualities of the rubber substance.

Chemical analysis has hitherto been subordinate in the commercial evaluation of rubber, partly on account of lack of exact knowledge regarding the nature of the secondary products (resins, nitrogenous substances, etc.), and partly owing to the absence of specific information on the influence exercised by them on the vulcanization process on the one hand, and on the more important attributes (strength, elasticity, etc.), on the other hand.

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<sup>4</sup> Philip Schidrowitz, Ph.D., the "Analyst," May, 1915—"Recent Advances in the Analyses and Evaluation of Rubber and Rubber Goods."

If the difficulties associated with the chemical investigation of the nature and influence of the "impurities" necessarily make progress in this direction slow, it is not surprising that the work having as its object the identification and evaluation by chemical means of different rubber substances or caoutchoucs is still in a more or less embryonic state.

Recent work by Caspari suggests the possibility of discriminating, up to a point, by physico-chemical methods, between caoutchoucs of different commercial quality. According to Caspari, rubber is of a composite character and consists of (1) "soluble" rubber, which is a weak but elastic colloid, soluble in light petroleum, and (2) of "insoluble" or "pectous" rubber, which is an elastic colloid of considerable mechanical strength. The latter, in some respects resembling a slightly vulcanized material, preserves its structure on contact with solvents. It is, however, gradually dissolved by benzene and carbon tetrachloride, but whereas the viscosities of the soluble in Brazilian and plantation Para, respectively, are very similar, the "pectous" in the latter is far more readily attacked by benzene or carbon tetrachloride than the "pectous" of the former. According to Caspari, Brazilian fine contains 35 to 50 per cent. of "pectous," whereas plantation rubber examined by him showed no more than 10 to 25 per cent. Caspari believes that "nerve" or strength is mainly due to the "pectous" variety. The work of Caspari will require confirmation and amplification before it is applied to rubber evaluation. It suggests a new field of research, indicating the possibility of estimating the quality by a direct physico-chemical method.

SECONDARY PRODUCTS—RUBBER RESINS—The outstanding feature of the work of Heinrichsen and Marcusson is that all resins, excepting that from Para (*Hevea*), are optically active. In certain cases, therefore, the absence of optical activity in the extracted resin may be taken as evidence that no rubber other than *Hevea* is present. Para resin contains 15 per cent. and other resins up to 100 per cent. of unsaponifiable matter. The optical activity appears to be mainly due to the latter. Iodine values varying from 30.6 for jelutong resin to 118 for Para resin were found. So far as the investigation has been carried

it appears that the resins from vulcanized rubber exhibit the same characteristics as those from the crude material. D. Bloom, as the result of the examination of 150 samples of resin from different species, concluded that the "acid value" of the resin from the same species is constant.

The effect of rubber resin on vulcanizing capacity is a matter of controversy. Litharge has been shown to be practically inoperative as a catalyst in the absence of rubber resins. Where litharge or other catalyst was not employed it has been found that the rubber resins do not exercise any marked effect on the curing capacity.

MECHANICAL IMPURITIES.—Beadle and Stevens give the following method (for these materials only). They "depolymerize" the rubber by heating with a solvent of high boiling point, thinning still further with a solvent of low viscosity, filtering and weighing.

INSOLUBLE MATTER—NITROGENOUS SUBSTANCES.—This item does not apply to accidental mechanical impurities, but to natural and normal substances always present to some extent in crude rubber. While there is no proof that normal "insoluble" is essentially a nitrogen product (a part doubtless consisting of oxidation products) it is fairly certain that it normally contains a high proportion of nitrogen.

Schmitz's method, 2.5 grams rubber, treated with 50 c.c. pentachlorethane for five to seven hours at 85 to 90 degrees C. with the formation of very fluid solution readily filterable, particularly if somewhat diluted with chloroform. The residue can be further purified by dissolving in five per cent. solution of sodium hydroxide and reprecipitating with hydrochloric acid.

PRACTICAL CONSIDERATIONS.—There is considerable evidence to warrant the assumption that the "insoluble" matter in crude rubber has an important bearing on vulcanizing capacity, but no quantitative relation has been discovered. While it has been shown that the removal of the "insoluble" markedly decreases curing capacity, the experience of the author is that rubbers with low proportions of "insoluble" do not necessarily cure badly, nor do samples with high "insoluble" necessarily cure

rapidly. Probably "insoluble" varies so in composition that further methods of separation must be devised before "insoluble" can be taken as a criterion of quality. The author prefers the indirect method for determining "insoluble," which consists in evaporating a convenient volume of clear solution, obtained by treating 0.5 to one gram of rubber with 100 to 200 c.c. benzene in a tall cylinder, allowing to settle and weighing the residue in a pipetted portion drawn off from above the residue.

ESTIMATION OF RUBBER.—Assuming a satisfactory method of separating the "insoluble" matter, the most satisfactory indirect method of estimating rubber is by deducting the sum of moisture plus resin plus "insoluble" from 100. This method involves the assumption that the whole of the ash and nitrogen is present in insoluble form. The author recommends the return of the analysis in the following form:

Moisture .....	Per cent.
Resin (acetone extract) .....	"
Insoluble matter .....	"
Rubber (difference) .....	"
The above contains:	
Ash (mineral matter) .....	"
Nitrogen .....	"
Nitrogen = protein .....	"

These notes apply only to routine technical analysis of which the chief object is to ascertain whether a distinct abnormality is disclosed and to control methods of production or of gauging suitability for specific manufacturing purposes.

DIRECT METHOD BY TETRABROMIDE FOR DETERMINING RUBBER.—The reader is referred for details of this method to the work by Caspari on "Laboratory Methods for Rubber Analysis."

The reaction of bromine on caoutchouc is  $C_{10}H_{16} + 6Br = C_{10}H_{14}Br_4 + 2HBr$ .

ESTIMATION OF MOISTURE.—The best method is (1) to dry in water oven at 98 degrees C. till an increase in weight becomes apparent or for a standard time of two hours, or (2) to take the difference between original weight of sample and weight after acetone extract plus the extract.



WASHING LOSS.—It is generally agreed that if the sample is large and requires washing the analytical determination should be carried out on the washed, air-dried material.

#### PHYSICAL AND MECHANICAL TESTS.

VISCOSITY.—A low viscosity almost invariably indicates poor quality. A determination of swelling capacity (per Caspari) may give more satisfactory results.

ADHESIVE TEST.—Beadle and Stevens determine the load required to separate pieces of paper evenly coated with a solution of rubber. The paper is coated by drawing it over the surface of a five per cent. (or less) solution.

MECHANICAL TESTS.—By this is meant tensile tests. These are of no value as applied to raw rubber.

VULCANIZATION TESTS.—(a) Material. State of aggregation (degree of polymerization) or physical condition of the rubber substance, quality and nature of resin, and of “insoluble” matter and acidity.

(b) Process. Temperature, duration of cure, method of heating, quantity of sulphur; and if fillers are used, their nature and quantity. So long as our knowledge of the physical and chemical nature of the impurities and of the rubber substances is incomplete it is impossible to devise any method of analysis or physical test which will enable us to determine quantitatively the effect of the various factors on vulcanization. Direct vulcanization tests are, therefore, for the present, essential for the purpose of practical evaluation. Broadly stated such may comprise: (a) observations on material during or rather towards the process; (b) observations on the nature of the vulcanized product, with regard to “rate of cure,” relying on the mechanical properties of the cured stock.

There appears to be no direct connection between the “co-efficient of vulcanization” and the technical properties of the material. Various types of tensile tests have been devised and are applied to vulcanized rubber. There is an essential difference between tests for the comparative evaluation of crude rubber and tests applied with the view of examining the specific properties of any given rubber article. With regard to the former it is desirable to use methods calculated to measure cer-

tain intrinsic and typical properties of the raw material, such as curing capacity, strength, distensibility and capacity for recovering.

Any system of evaluation based on factors influencing the vulcanization process must be carried out under standardized conditions of mixture, cure and test. Pure rubber and sulphur are considered the best, because most uniform and also because a filler renders the reaction less delicate.

#### THE ANALYSIS OF VULCANIZED RUBBER.

THE pioneer work of rubber analysis was done by Dr. Robert Henriques and Dr. Carl Otto Weber. Following these distinguished chemists others have worked on the problems and as a result there is available an excellent selection of reliable analytic methods. Standard methods have been adopted for specification purposes by the United States Bureau of Standards, Washington, District of Columbia; American Society for Testing Materials, Philadelphia, Pennsylvania; National Board of Fire Underwriters' Laboratories, Chicago, Illinois; Joint Rubber Insulation Committee, American Institute of Electrical Engineers.

A complete analysis of vulcanized rubber includes:

1. Acetone extract: (a) free sulphur, (b) waxes.
2. Chloroform extract, mineral rubber, tar or asphalt.
3. Alcoholic potash extract, rubber substitutes.
4. Total sulphur.
5. Ash and mineral analysis.
6. Rubber.
7. Specific gravity.

#### REMARKS ON ANALYSIS.

The following remarks in explanation of the analysis are from Circular 38 on "Testing of Rubber Goods," by the United States Bureau of Standards.

ACETONE EXTRACT.—Acetone extracts the rubber resins, the free sulphur, and any mineral oils or waxes that may have been used. The difference in amount between the total acetone extract and the free sulphur present indicates something regarding the quality of the rubber present. For the best grades

of Para rubber this should not exceed five per cent. of the rubber. The presence of mineral oil indicates the possibility of reclaimed rubber having been used.

**FREE SULPHUR.**—The free sulphur is that part of the sulphur originally added as such which remains unchanged after vulcanization. Small amounts of free sulphur are not harmful and it is difficult to place a limit beyond which it is to be considered excessive. A limit is usually placed on the free sulphur in high-grade insulation compounds, chiefly because it may corrode the copper wire.

**TOTAL SULPHUR.**—Sulphur occurs in vulcanized rubber as free sulphur, in combination with the rubber, and at times in the mineral fillers, reclaimed rubber, and rubber substitutes. It is limited in specification in high-grade material in order to eliminate undesirable sulphur minerals and prevent as far as possible the use of inferior or reclaimed rubbers and rubber substitutes. The inferior rubbers require a larger percentage of sulphur than Para for proper vulcanization, while reclaimed rubber and substitutes contain usually large amounts of sulphur.

**ASH AND SULPHUR IN THE ASH.**—The ash or residue after ignition, consists principally of the non-volatile mineral fillers. It is used in calculation of the rubber by difference. The sulphur in the ash is determined merely for the purpose of obtaining a correction figure and has no other significance.

**BARYTES.**—There is no objection to the sulphur presence in mineral fillers, provided the mineral containing it has no injurious effect on the rubber, and that amount of such sulphur may be readily determined. Barytes is such a substance and is permitted in practically all compounds where the amount of sulphur is limited by specifications. There are no other fillers which as yet fulfil both of the conditions named.

**RUBBER.**—The determination of the amount of rubber present in a vulcanized compound is both important and difficult. The procedure extensively used is to calculate the percentage of rubber by the difference between 100 per cent. and the sum of the ash (sulphur free), total sulphur, and corrected acetone extract. It is as good as any method yet devised, although not always accurate.

**SPECIFIC GRAVITY.**—It is apparent that with equal percentages by weight of ingredients, a compound of a given specific gravity will have less rubber per unit volume than one of higher specific gravity. In order to insure a minimum volume of rubber, specific gravity limits are stated.

**CHLOROFORM EXTRACT.**—The so-called mineral rubbers, such as tar, bituminous substances, elaterite, gilsonite, etc., are used extensively as rubber substitutes. These substances are partly soluble in acetone, but the material so removed is not characteristic of these substitutes and not readily distinguished from vaseline and similar mineral oils. Part of the insoluble portion remaining after the treatment with acetone is soluble in chloroform, the solution being very dark in color. Properly vulcanized high-grade rubbers yield only a small amount during the chloroform extraction, the solution being practically colorless.

**ALCOHOLIC-POTASH EXTRACT.**—Some rubber substitutes are prepared by the action of sulphur or sulphur chloride on vegetable oils. Alcoholic-potash extraction detects the presence of such substitutes and gives some idea of the amount. Para rubber contains only a small percentage of material extracted by this solvent.

#### BUREAU OF STANDARDS' METHODS OF ANALYSIS.

##### PREPARATION OF SAMPLES.

(1) **SOFT RUBBER**—A sample of not less than 25 grams shall be prepared by taking pieces from various parts of the original sample. With those having cover and tube, separate samples of each shall be made. From fire hose remove the backing before grinding.

(2) **GRINDING.**—The sample shall be cut into small pieces and then run through a grinder, taking for analysis only such material as will pass a 20-mesh sieve. Care must be taken to see that the grinder does not become appreciably warm during the grinding. If the nature of the material is such that it gums together so that it will not pass through the sieve (as would be the case with under-vulcanized samples), it will be sufficient to pass the material through the grinder twice and accept all the material for the finer sample.

(3) **HARD RUBBER.**—Samples of this material shall be prepared for analysis by rasping.

(4) **REAGENTS.**—All reagents shall be of the chemically pure quality, specially tested before use.

(5) **ACETONE** shall be freshly distilled over anhydrous potassium carbonate, using the fraction obtained at 56 degrees to 57 degrees C.

(6) **ALCOHOLIC POTASH.**—Shall be of normal strength, made by dissolving the required amount of potassium hydroxide in absolute alcohol and allowing it to settle. Only the clear solution shall be used.

(7) **THE NITRIC ACID-BROMINE REAGENT** shall be prepared by adding a considerable excess of bromine to concentrated nitric acid, shaking thoroughly, and allowing it to stand for some hours before using.

(8) **THE FUSION MIXTURE** for sulphur determinations shall be made by mixing equal quantities of sodium carbonate and powdered potassium-nitrate.

(9) **BARIUM-CHLORIDE SOLUTION** shall be made by dissolving 100 grams of barium chloride in one liter of distilled water and adding two or three drops of concentrated hydrochloric acid. If there is any insoluble matter of cloudiness, the solution shall be heated on the steam bath overnight and filtered through 589 Schleicher and Schull blue-ribbon filter paper.

#### ANALYSIS OF MECHANICAL GOODS.

(10) **ACETONE EXTRACT.**—Place a 2-gram sample in an acetone-extracted Schleicher and Schull paper thimble and extract continuously with acetone for eight hours, unless the solution in the thimble is still colored at the end of that time, when the extraction shall proceed the next day for a further period of four hours. Transfer the extract to a tared 100 or 150 c.c. Erlenmeyer flask, using chloroform or benzene for dissolving any material which may have been separated from the solvent during the course of the extraction. Drive off the solvents at as low a temperature as possible, using a gentle current of air. Dry the flask and contents in an air bath at 90 degrees to 95 degrees



C.; cool and weigh. Call the residue "acetone extract, uncorrected." Calculate the results to percentage.

(11) **FREE SULPHUR.**—Add to the flask (paragraph 10) containing the acetone extract, uncorrected, 50 to 60 c.c. of distilled water and two or three c.c. of bromine. (If the acetone extract indicates a large amount of free sulphur, the amount of bromine used may be increased.) Heat gently on the steam bath until the solution is practically colorless, and filter into a 250-c.c. beaker. Cover the beaker with a watch glass, heat to boiling on the steam bath, add 10 c.c. of 10 per cent. barium chloride solution, and allow the precipitate to stand overnight. The next day filter the precipitate on an 11 cm. 590 Schleicher and Schull filter paper. Ignite in a small porcelain crucible, using a small Bunsen flame and not allowing the paper to inflame; cool and weigh. Calculate the barium sulphate to sulphur by means of the factor 0.1374, and calculate the percentage of free sulphur.

(12) **TOTAL SULPHUR.**—Place 0.5 grams of rubber in a porcelain crucible of about 100 c.c. capacity. Add 20 c.c. of the nitric acid-bromine mixture (paragraph 7), cover the crucible with a watch glass, and allow to stand for one hour. Heat very carefully for an hour, remove the cover, rinsing it with a little distilled water, and evaporate to dryness. Add five grams of fusion mixture (paragraph 8) and three to four c.c. of distilled water. Digest for a few minutes, and then spread the mixture half way up the side of the crucible to facilitate drying. Dry on a steam bath or hot plate. Fuse the mixture, using a sulphur-free flame, until all the organic matter has been destroyed and the melt is quite soft. Allow to cool, place the crucible in a 600-c.c. beaker, and cover with distilled water. Digest three or four hours on the steam bath. Filter into a 800-c.c. beaker, washing thoroughly with hot water. The total volume should be about 500 c.c. Add seven to eight c.c. concentrated hydrochloric acid to the filtrate, and heat on the steam bath. Test the solution for acidity with congo paper, add 10 c.c. of 10 per cent. barium chloride solution, and allow to stand overnight. Filter barium sulphate as before. Calculate to percentage of sulphur present.

(13) **ASH.**—Wrap a 1-gram sample in an 11-cm. 590 Schleicher and Schull filter paper, and after extracting with ace-

tone for four hours transfer to a medium-sized porcelain crucible and ignite at the lowest possible temperature; cool and weigh.

(14) **SULPHUR OF ASH.**—Add a few drops of concentrated nitric acid to the ash (paragraph 13), stir with a small glass rod and evaporate off the excess acid on the steam bath. Add five grams of fusion mixture (paragraph 8) and heat until fused. When cool, place the crucible in a 400-c.c. beaker, cover with water, and heat on the steam bath for two or three hours. Filter into a 600-c.c. beaker (reserve the insoluble residue for testing according to paragraph 15), add seven to eight c.c. concentrated hydrochloric acid to the filtrate, cover, and heat to boiling on the steam bath. Add 10 c.c. of 10 per cent. barium chloride solution, and allow to stand overnight. Treat the barium sulphate precipitate as under paragraph 11. Calculate the sulphur by the factor 0.1374.

(15) **BARYTES.**—In case the total sulphur is limited by specification and barytes is permitted as a filler, the latter must be determined, since the sulphur present in this mineral must be deducted from the total sulphur. The barytes is calculated from the barium in the ash, determined as follows: filter off the insoluble matter after the fusion and extraction in paragraph 14, wash back into the original beaker with hot water, add five c.c. of 10 per cent. hydrochloric acid, and heat the solution on the steam bath until as much as possible is dissolved. Filter through the same filter as before, washing thoroughly with hot water. Nearly neutralize the solution with sodium carbonate, leaving it slightly acid. Saturate the solution with hydrogen sulphide, and when the lead sulphide has settled filter into a 400-c.c. beaker and wash thoroughly. The total volume should not be over 200 c.c. Cover the beaker containing the filtrate, heat to boiling, and add 10 c.c. of 10 per cent. sulphuric acid. Allow the precipitate to stand overnight. Filter off the barium sulphate as directed in paragraph 11. Calculate the percentage of barytes. Then calculate the percentage of sulphur in the barytes by the factor 0.1374.

(16) **CALCULATIONS.**—(a) Subtract the free sulphur from the "acetone extract uncorrected," and report the differ-

ence as "acetone extract corrected." (b) Subtract the sulphur in the ash from the ash as determined in paragraph 13, and report "ash, sulphur-free." (c) Subtract from the total sulphur determined according to paragraph 12, the percentage of sulphur present as barytes, if the latter determination has been made (see paragraph 15), and report the difference as "total sulphur corrected." Then add the sulphur so deducted to the ash, in this case reporting the latter simply as "ash corrected." In other words, only the sulphur other than that in barytes will be deducted from the ash when the total sulphur is corrected for barytes. (d) Subtract from 100 per cent. the sum of the "acetone extract corrected," total sulphur (corrected or not, as the case may be), and ash (sulphur-free, or corrected for sulphur other than barytes), and call the remainder "rubber by difference." (e) Divide the "acetone extract corrected" by the sum of the "acetone extract corrected" and the "rubber by difference" and call the result "ratio, acetone extract to rubber." It will be simpler to express the results in percentages. When new rubber only is used this will give the percentage of acetone-soluble matter in the rubber.

(17) SPECIFIC GRAVITY.—Make this determination in a pycnometer, using about 5 grams of rubber cut into small strips, taking care to avoid having air bubbles adhering to the rubber. Do not use a ground sample for this determination, since it is intended to determine the specific gravity of the compound as a whole. Aside from the difficulty of completely removing air bubbles, the specific gravity of a sample which is at all porous will be, after grinding, higher than when this is determined on strips. Calculate the specific gravity on the basis of water at 15 degrees C as 1.00.

(18) ALCOHOLIC-POTASH EXTRACT.—Fire hose, tested according to the National Board of Fire Underwriters' specifications, calls for an alcoholic-potash extraction. It is performed on the dried rubber remaining after the acetone extraction. Complete method appears in paragraph 28.

#### ANALYSIS OF 30 PER CENT. PARA INSULATION.

(19) GENERAL.—The determinations to be made on high-grade insulation compounds are acetone extract, unsaponifiable

matter, waxy hydrocarbons, free sulphur, ash, and total sulphur, and sometimes alcoholic-potash and chloroform extracts.

(20) ACETONE EXTRACT.—Determine as under paragraph 10.

(21) UNSAPONIFIABLE MATTER.—Add to the acetone extract (paragraph 20) 50 c.c. normal alcoholic potash (paragraph 6), heat on steam bath under a reflux condenser for two hours; remove the condenser and evaporate to dryness. Transfer to a separatory funnel, using about 100 c.c. water; add 25 c.c. ether, and shake. Allow the two layers to separate thoroughly, then draw off the water layer. Continue the extraction of the water layer with fresh portions of ether until the ether will no longer remove any unsaponifiable matter; unite the ethereal layers, and wash with distilled water, adding the first wash water to the extracted aqueous layer. This aqueous solution is reserved for the free sulphur determination (paragraph 23). Transfer the ether to a tared Erlenmeyer flask, distil off the ether, dry at 90 degrees to 95 degrees C.; cool and weigh.

(22) WAXY HYDROCARBONS.—To the unsaponifiable matter (paragraph 21) add 50 c.c. absolute alcohol and heat on the steam bath for one-half hour. Place the flask in a mixture of ice and salt and let stand for one hour. Filter off the separated waxy hydrocarbons, using Schleicher and Schull 589 blue-ribbon filter paper, and applying a gentle suction. Wash with alcohol which has been cooled in an ice-salt mixture. The funnel should be surrounded by a freezing mixture in order that the temperature may not rise during filtration. Dissolve the precipitate from the filter paper with hot chloroform, catching the solution in a weighed 100 to 150-c.c. beaker. Wash the flask with hot chloroform and add the washings to the same beaker, in order to include any insoluble matter adhering to the walls of the flask. Evaporate off the solvent, dry the residue at 90 degrees to 95 degrees C., cool and weigh.

(23) FREE SULPHUR.—Transfer the aqueous solution (paragraph 21) to a 250-c.c. beaker, and heat on the steam bath until the ether has been removed. Add 25 c.c. bromine water, heat one hour, add five c.c. concentrated hydrochloric acid, and

heat until the excess of bromine has been driven off. (Test for acidity with congo paper; the amount of acid specified is sufficient if instructions are followed exactly, and a large excess of acid is to be avoided.) Filter into a 250-c.c. beaker, add 10 c.c. 10 per cent. barium chloride solution and finish the determination as under paragraph 11.

(24) ASH.—Proceed as under paragraphs 13 and 14.

(25) TOTAL SULPHUR.—Proceed as under paragraph 12. There will be no correction for barytes.

(26) CALCULATIONS.—(a) Subtract the sum of the “free sulphur” and “waxy hydrocarbons” from the “acetone extract uncorrected,” and report the difference as “acetone extract corrected.” (b) Subtract from 100 per cent. the sum of the “acetone extract corrected,” “waxy hydrocarbons,” “ash sulphur-free,” and “total sulphur” and report the results as “rubber by difference.” (c) Divide the “acetone extract corrected” by the sum of the “acetone extract corrected” and the “rubber by difference” and report the results under “ratio, acetone extract to rubber,” as under paragraph 16 (e).

(27) CHLOROFORM EXTRACT.—Without removing the adhering acetone from the rubber (paragraph 20) extract with chloroform for four hours. Evaporate off the solvent in a weighed flask or beaker, dry at 90 degrees to 95 degrees C., cool and weigh. Reserve the rubber for the alcoholic-potash determination.

(28) ALCOHOLIC-POTASH EXTRACT.—Dry the rubber (paragraphs 10, 18, and 27) at about 50 degrees to 60 degrees C., transfer to a 200-c.c. Erlenmeyer flask, add 50 c.c. alcoholic-potash solution, and heat under a reflux condenser for four hours. Filter through a folded filter into a 250-c.c. beaker, washing with 50 c.c. of 95 per cent. alcohol, and then 50 c.c. of boiling water. Evaporate the filtrate to dryness. Transfer the residue to a separatory funnel, using about 75 c.c. of distilled water. Add a few drops of methyl orange, and acidify the solution with 10 per cent. hydrochloric acid. Extract with four portions of ether, 25 c.c. each, unless the fourth portion should be colored, when the extraction should be continued until no further quantity can be extracted. Unite the other



fractions, wash thoroughly with distilled water, and evaporate the ether in a weighed beaker. Dry at 90 degrees to 95 degrees C., cool and weigh.

The methods of rubber analysis specified by The American Society for Testing Materials, the National Board of Fire Underwriters' Laboratories, and the Joint Rubber Insulation Committee in general closely resemble those recommended by the United States Bureau of Standards. The Cottle extracting apparatus is specified in place of the all-glass apparatus of the Bureau of Standards.

#### JOINT RUBBER INSULATION COMMITTEE'S METHODS.

The percentage of rubber shall be considered to be the difference between 100 and the sum of the total sulphur and ash expressed as percentages and figured on the total compound. If the alcoholic-potash extract is over two per cent. of the rubber as first calculated, subtract this excess also from the rubber. The organic-acetone extract shall be obtained by taking the difference between the total acetone extract and the free sulphur. The organic acetone extract, free sulphur, total sulphur and alcoholic-potash extract shall be figured on the amount of gum as found by the above procedure.

A general outline of the procedure is given on following page. It will be seen that the residues from the alcoholic-potash saponification are treated with hydrochloric acid to remove organic matter, and the part insoluble in acid is dried and divided into two parts, one of which is used for the determination of sulphur, and the other ignited. A sulphur determination is also made on the ash. The rubber hydrocarbons as a percentage of the total sample are given by the following formula:

$$\text{Rubber Hydrocarbons} = 100 \frac{C}{4} \left[ 1 - \frac{E-F}{D} - \frac{H}{G} \right]$$

The total weight of sample used in the determination is four grams and the letters *C*, *D*, *E*, *F*, *G*, and *H* represent the weights in grams of the substance in the diagram.



ANILINE METHOD FOR DETERMINATION OF MINERAL FILLERS IN RUBBER.<sup>5</sup>

ALTHOUGH the use of aniline as a solvent for vulcanized rubber is not new, there is very little information to be found concerning it in the literature. The following method is of much interest:

In making the determination it is essential that the sample be finely powdered (20 mesh). A one-gram sample is extracted with acetone for four hours, dried at a low temperature, and then transferred to a weighed 100 c.c. centrifuge tube. It is covered with 50 c.c. of pure aniline and 5 c.c. of nitrobenzene, stirred, covered, and heated at 160 degrees C., with occasional stirring until solution is complete.

It is our practice to heat the samples overnight in a Freas oven, and in most cases the samples are completely dissolved by the next day. Sometimes the sample dissolves in three to four hours. If the rubber is not yet in solution, it can be seen by stirring with a glass rod. When solution is complete, there is nothing to be seen but fine pigment, free from rubbery appearance.

The chemist who makes the analysis for the first time may be uncertain of himself at this point, but after one or two determinations have been made he will at once recognize any undissolved rubber.

The tube is allowed to cool sufficiently, filled up with ether and well stirred. It is then centrifuged for 15 minutes at 1,500 R.P.M.

The supernatant liquid is decanted, about 25 c.c. of ether added and the pigment stirred up completely. It is centrifuged again and the decantate added to the first. Four washings with ether are sufficient. The tube is dried at 100 degrees C., cooled and weighed. The united decantates are evaporated and then ignited in a weighed porcelain or silica dish. The weight of fillers in it is added to that in the tube.

The percentage of fillers plus that of total acetone extract is subtracted from 100 per cent., and the difference recorded in rubber gum.

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<sup>5</sup> Otto H. Klein, John H. Link, and Frank Gottsch—"Aniline Method for Determination of Mineral Fillers in Rubber." American Chemical Society Proceedings, September, 1916.

Aniline differs from other solvents in that rubber dissolved in it forms a thin solution which permits the mineral fillers to separate readily.

The small amount of nitrobenzene is used, because it makes solution more rapid. Semi-cured compounds dissolve more slowly than thoroughly cured soft stocks or very hard ones. With under-cured compounds, a soft, pasty mass is formed, which is very slow to dissolve, while this does not occur if the material is properly vulcanized.

In some few cases an additional digestion with half the quantity of solvent for five hours will reduce the amount of mineral fillers about 0.5 per cent. In specification work it is advisable to make this second digestion after the ether has been expelled from the tube by heating.

Analysis of the fillers shows that the rubber as found by difference will not include the sulphur of vulcanization.

The sum of the percentages of rubber found and organic acetone extract is slightly greater than the percentage of rubber used in the recipe.

The fillers during vulcanization and afterwards in the course of analysis have combined with sulphur to form new compounds. If this combination of fillers and sulphur is a substitution of sulphur for some other acid radical, the resultant product would weigh less than the sum of the ingredients entering the reaction and the rubber found by difference would be slightly greater thereby.

#### DIRECT DETERMINATION OF RUBBER BY WET COMBUSTION.<sup>6</sup>

THE rubber nitrosite for combustion is prepared as follows:—After the rubber sample has been ground in a meat-chopper to pass a 20-mesh sieve, and a  $\frac{1}{2}$  gram of it extracted 3 hours with acetone, and  $\frac{1}{2}$  hour or longer with chloroform, the extracted sample is allowed to dissolve in, or thoroughly absorb, chloroform. A small Florence flask (75 c.c.) is used, which may be about one-half full of the solvent. Nitrous oxide vapors, evolved from dilute nitric acid (specific gravity 1.3)

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<sup>6</sup> L. G. Wesson and E. S. Knorr. "Wet Combustion in the Nitrosite-Combustion Method for the Direct Determination of Rubber." American Chemical Society Proceedings, September, 1916.

and arsenic trioxide, are then passed through the cooled chloroform until the deep-green color becomes permanent for, say 15 minutes, and the whole allowed to stand overnight for completion of the action.

The chloroform is then decanted through a dry Gooch crucible and asbestos mat (the former rests in an ordinary 60-degree filter funnel) into the combustion flask, from which the chloroform is then evaporated by means of a boiling-water bath and a dry-air current.<sup>7</sup>

Meanwhile the residue in the Florence flask has been similarly dried. The separation of fillers and nitrosite is now brought about in the following way: Small portions (5 c.c.) of calcium chloride-dried ethyl acetate are added to the residue in the Florence flask, the latter warmed, and the liquid decanted through the Gooch crucible into the combustion flask, repeatedly, until the filtrate runs through entirely colorless. After evaporation of the acetate (recovery of the solvent as well) the residue is carefully freed from solvent by warming the containing flask in a boiling water bath for, say, 15 minutes, after which 15 c.c. of water containing 1 drop concentrated HCl, are added, and quickly evaporated by the use of a boiling calcium chloride bath and brisk current of dry air. The heating is continued at least one-half hour after the residue is again apparently dry.

The combustion apparatus consists of a 200 c.c. round-bottomed distilling flask, which is provided with a dropping funnel (100 c.c.) through a one-holed rubber stopper, and a series of U-tubes containing in order: (1) concentrated  $\text{H}_2\text{SO}_4$ — $\text{K}_2\text{Cr}_2\text{O}_7$ , renewed every 1 or 2 combustions; (2) water containing a drop of the preceding; (3) granular zinc; (4) calcium chloride; (5) soda-lime (weighed); (6) soda-lime and calcium chloride (weighed).

The combustion is conducted as follows: The weighed soda-lime tubes in position, and the combustion flask cooled by water, a volume (20 c.c.) of cooled concentrated sulphuric acid is run rapidly into the flask on the nitrosite; then the cooled

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<sup>7</sup> J. B. Tuttle, of the Bureau of Standards, has found that the chloroform-soluble residue thus recovered may be very appreciable, and it is to his suggestion that this modification is due.



oxidizing solution of 10 grams pulverized  $K_2Cr_2O_7$  in 75 c.c. concentrated  $H_2SO_4$  in a very slow stream. The flask may now be gently warmed by a sand bath to obtain a moderately rapid evolution of gas.<sup>8</sup>

This is done as long as gas continues to be evolved (about one hour), when a carbon dioxide free current of air, the heating being maintained, is passed via the dropping funnel through the apparatus for at least one-half hour to sweep all carbon dioxide into the soda-lime tubes.

$$\text{Weight } CO_2 \times \frac{136}{440} \times 200 \text{ gives percentage } C_{16}H_{16} \text{ in the sample.}$$

We hope, in conclusion, that further study and improvements of this method will eventually give a reliable and not too difficult procedure for the direct determination of rubber, not only in good quality compounds, but also in factice and other inferior substitute-containing rubbers.

#### SULPHIDE SULPHUR.

The presence of metallic sulphides and sulphates in technical rubber articles complicates the estimation of the "combined" sulphur. Ordinarily the free sulphur and that present as substitute are extracted with acetone and alcoholic potash, respectively. In the absence of sulphides and sulphates an estimation of sulphur in the residue gives the percentage in combination with the rubber. In the presence of sulphides and sulphates it is usual to heat a portion of the residue with high boiling point solvents to destroy the rubber and render it soluble. The sulphur is then estimated in the washed mineral residue. The sulphur is also estimated in another portion of the extracted rubber, and the sulphur combined with the rubber estimated by difference.

The method is unsatisfactory and has two disadvantages. First, many vulcanized rubbers are decomposed with difficulty. They carbonize and cake even at carefully regulated temperatures. Consequently the residue, after washing with benzene,

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<sup>8</sup> That carbon monoxide is formed during the combustion can be shown by allowing the gases which have passed the absorption train to come in contact with heated copper oxide and then barium hydroxide solution. A precipitate ensues, but the amount is not appreciable for the results of the analysis.

contains undissolved organic matter which protects the decomposition of the mineral sulphides. Second, the method assumes that the vulcanized rubber does not react with basic substances, such as litharge or magnesia, present in the mixing during heating, with formation of metallic sulphides, although vulcanizing temperatures are employed.

The method described below is due to H. P. Stevens and is applicable to those sulphides decomposable by heating with acids. It is, therefore, suitable for the estimation of the sulphides of zinc and lead. The metallic sulphides in either vulcanized or unvulcanized rubbers are so protected by the rubber surrounding the mineral particles that the surface only is attacked by prolonged boiling with strong hydrochloric acid solution. If the vulcanized rubber be first swollen in a suitable solvent in which the aqueous acid is partly soluble, the metallic sulphides of lead and zinc are easily and completely decomposed. Ordinary methylated ether has been found the most suitable solvent. If preferred, benzene or one of the chlorinated hydrocarbons, such as dichlorethylene, can be employed. Liberated hydrogen sulphide is estimated and calculated to percentage of sulphide sulphur.

Estimation of hydrogen sulphide by oxidation to sulphuric acid does not prove satisfactory. Best results are obtained by precipitation in lead acetate solution. The absorption is very complete in the first bottle. The freshly precipitated and washed sulphide is decomposed by shaking with iodine solution.

#### ESTIMATION OF SULPHIDE SULPHUR.

To determine the sulphide sulphur, 20 c.c. of concentrated hydrochloric acid and 30 c.c. of ether are placed in a Voigt's flask (a flask having a ground-in stopper carrying an outlet tube and a side-inlet tube which passes through the side of the flask and reaches nearly to the bottom). The air is expelled from the flask by a current of carbon dioxide. The flask is then connected with an absorption apparatus containing lead acetate solution and a weighed quantity of rubber is introduced. The rubber swells gradually and after about 15 minutes the ether, together with evolved hydrogen sulphide, is driven over into the absorption apparatus by gentle heat. The decomposition is com-

pleted by boiling the mixture a few minutes. Traces of hydrogen sulphide are removed by a current of carbon dioxide and the lead sulphide is collected, washed and titrated iodometrically.

#### SULPHATE SULPHUR.

The residue in the Voigt flask, containing the sulphates is extracted repeatedly with hydrochloric acid and the sulphates determined as barium sulphate.

#### SOLVENTS FOR VULCANIZED RUBBER ANALYSIS.

Ether, in presence of hydrochloric acid, gradually dissolves vulcanized rubber at the ordinary temperature, and the dissolved rubber contains about 1.5 per cent. of sulphur. A mixture of benzene and hydrochloric acid also dissolves vulcanized rubber. Chlorohydrocarbons act similarly to the mixture of solvents and hydrochloric acids, but are no more rapid than a mixture of benzene and acids.

Douglas F. Twiss, in analytic work on rubber, finds that a mixture of equal parts by volume of concentrated hydrochloric acid and ether acts readily on rubber mixings at ordinary temperature, the penetration of the acid being facilitated by the swelling action of the ether.

Another application for this reagent is the neutralization of accelerators, such as litharge, before attempting the removal of free sulphur from rapid-curing mixings. Where necessary to examine the contents of combined sulphur in a partially cured rubber-mix which contains much mineral accelerator and free sulphur, the conversion of the accelerator into an inert substance before the acetone extraction has the advantage of removing the likelihood of vulcanization during extraction.

To effect such purpose the procedure used is to treat one to two grams of the rubber with the acid-ether reagent until this reagent penetrates throughout the mass. The progress of the action, in presence of litharge, is easily followed by the change in color. The change is usually completed in a day. The rubber mass can then be removed or the ether evaporated. The mass is next washed in running water and dried. It is then ready for acetone extraction and the combined sulphur estimated in the residual rubber. If mineral sulphates are absent,

the sulphur in the extracted rubber may be considered as organically combined sulphur. It is safer to begin with two samples and to estimate the total free and combined sulphur in one and free sulphur in the other. The above process appears to be desirable where there are large quantities of free sulphur and accelerator. In the opposite instance the method of Stevens is perfectly satisfactory.

#### MT. PROSPECT LABORATORY METHODS OF ANALYSIS.

The methods employed in the Mt. Prospect Laboratory Department of Water Supply, Gas and Electricity of the City of New York, possess novel features introduced by Frank Gottsch. These methods are as follows:

**FREE SULPHUR.**—The dried acetone extract is entirely transferred to a 60 c.c. iron or nickel crucible by acetone, chloroform or benzol, and the solvents evaporated off on the steam bath and 6 grams of potassium carbonate and four grams of sodium peroxide are added. Mix, cover, heat at low temperature over asbestos shield to avoid sulphur fumes, until the mixture fuses, then bring to quiet fusion for 15 to 20 minutes. Avoid rapid heating and explosion and rotate the melt while solidifying. When cool put crucible and cover into a casserole with 200 c.c. of water, add five to ten c.c. bromine water and boil melt till dissolved. Settle, decant, filter and wash through thick filter with hot water. Cool, acidify filtrate with dilute hydrochloric acid, make up to 400 c.c. and precipitate boiling with ten c.c. of ten per cent. solution of barium chloride.

**MINERAL FILLERS.**—A one-gram sample is extracted by acetone for four hours and the rubber dried in the water oven at 100 degrees C., until the odor of acetone is gone. Transfer the sample to a 100 c.c. beaker, burn the thimble to ash and add it to the beaker. Add 50 c.c. of clear molten salol and heat the beaker on the hot plate at a temperature of not less than 120 degrees, nor more than 150 degrees C., stirring occasionally until the rubber is apparently dissolved. After settling, transfer the liquid to a 200 c.c. beaker and if the residue in the small beaker contains particles of undissolved rubber more salol is added and solution completed. Stir two c.c. of a one per cent. solution of soluble cotton in amyl acetate into the warm liquid in the 200 c.c. beaker, cool and add redistilled turpentine until a good



"flock" has formed, adding at least 75 c.c. of turpentine with constant stirring. Allow the liquid to stand until the flock settles. The supernatant liquid is decanted and filtered by suction through an alundum crucible placed in a Spencer holder. Wash the flock by decantation with turpentine, filtering the latter; transfer the whole to the crucible, then dissolve carefully in a few c.c. of acetone, and wash the fillers with acetone, being careful not to allow the fillers to cover and clog the sides of the crucible. All beakers and the crucible are to be thoroughly washed with acetone. Dry to constant weight at 105 to 110 degrees C., cooling in a desiccator. Evaporate all the filtrate and washings, transfer to a weighed porcelain dish, burn off the organic matter. Add weight of residue to that of the fillers in the crucible and calculate as "mineral fillers."

FOREIGN ALCOHOLIC POTASH EXTRACT.—The dry rubber residue from the acetone extract is extracted with 50 c.c. of alcoholic potash, stoppered, in an air oven kept between 105 and 110 degrees C., for four hours. Cool, filter and wash the residue clean with hot absolute alcohol. Precipitate potassium chloride by acidifying filtrate strongly with hydrochloric acid, settle, filter and wash with hot chloroform and evaporate the filtrate on a steam bath till odor of hydrochloric acid just disappears. Take up residue with chloroform, filter and wash with hot chloroform into a beaker, and evaporate to dryness. If the residue is not oily or greasy to touch, it may be disregarded. If oily or greasy the residue is washed with small portions of 88 degrees Baumé naphtha, filtered through a washed plug of cotton into a small weighed beaker, evaporated and dried in water oven at 95 to 100 degrees C. in 15-minute periods until the weight is constant, or increases. The result is calculated as "foreign alcoholic-potash extract."

VULCANIZED RUBBER GUM BY WEIGHT.—Subtract the sum of the percentages of free sulphur, organic acetone extract, mineral fillers and corrected foreign matter from 100 per cent. The balance is the vulcanized rubber gum by weight.

VULCANIZED RUBBER GUM BY VOLUME.—Multiply the percentage by weight of vulcanized rubber gum by the specific gravity. The product is that specified by the term vulcanized rubber gum by volume.



The method for free sulphur is designed to obviate absolutely the influence of organic matter by its complete removal. Concerning estimation of mineral fillers, it is found that salol will dissolve soft rubbers in less than an hour and vulcanite in from two to three hours. Owing to the condition of extreme fineness met with in many of the mineral fillers of rubber a coagulant is necessary to filter them off, even through an alundum crucible. Such a coagulant is soluble cotton dissolved in amyl acetate. Turpentine satisfactorily reprecipitates the soluble cotton used to form a flock suitable for filtration.

DETERMINATION OF TOTAL SULPHUR IN RUBBER.—The following method was devised by Dr. Ludwig Rosenstein:

Weigh out exactly 0.5 grams of the finely ground sample in a 300 c.c. Erlenmeyer flask. Add 15 c.c. of a saturated solution of arsenic acid, 10 c.c. of fuming nitric acid and 3 c.c. of saturated bromine water. Cover with a watch glass and boil until the sample is completely oxidized and a clear solution is obtained, adding more fuming nitric if necessary to complete the oxidation. Evaporate to syrupy condition, then add a few crystals of potassium chlorate to insure complete oxidation and to expel oxides of nitrogen. Continue the evaporation almost to dryness to insure complete expulsion of oxides of nitrogen. Cool and take up with 50 c.c. of 10 per cent. hydrochloric acid, heat on steam bath until solution is complete, filter to free from any insoluble matter and dilute the filtrate to about 300 c.c. From this solution the sulphur, which has been converted to sulphate, may be precipitated with barium chloride. Filter and weigh, observing the usual procedure and take special precaution that precipitate be filtered from the hot solution and washed with hot water to remove any lead salts.

The function of the arsenic acid is to raise the boiling point of the solution during the oxidation, thus making it more complete and rapid. It may be prepared by adding C. P. arsenic oxide to boiling water until boiling point of the solution is 140 degrees C.

This method has been found rapid and accurate to within less than 0.1 per cent. on rubber mixings, both cured and uncured containing known amount of sulphur, with and without various compounding ingredients.

## ELECTROLYTIC METHODS.

**ELECTROLYTIC METHOD FOR LEAD AND ZINC IN VULCANIZED RUBBER.**—The following method is by Elmer D. Donaldson. The portion relating to the deposition of zinc on platinum direct is adapted from a method by W. S. Kimley.

Donaldson's method consists of digestion of the ash in nitric acid and precipitation of lead as peroxide ( $\text{PbO}_2$ ), followed by evaporation and precipitation of zinc as metal, both on platinum. The electrolytic apparatus was equipped with a rotating electrode and pole-reversing switch. The larger electrodes were of platinum gauze  $1\frac{1}{2}$  inches wide by 2 inches high, sand blasted, and the rotating gauze  $\frac{1}{2}$  inch wide by 2 inches high. The apparatus was connected to a 110-volt direct current generator and lamp resistance.

*Lead.*—Weigh one gram rubber, wrap in a seven-centimeter ashless paper and incinerate in a 20 to 30 c.c. porcelain crucible. Brush the ash into a 200 c.c. electrolytic beaker, add 25 c.c. concentrated nitric acid, and digest on hot plate for 15 minutes. Boil to expel nitrous fumes and dilute to about 125 c.c., having solution at 158 degrees to 176 degrees F. Electrolyze with rotating cathode, using direct current of two to three amperes. The lead will appear on the large gauze anode as peroxide, black when in large amounts, bronze colored when in small amounts. Electrolyze 30 minutes and wash anode thoroughly with water to remove mechanical impurities, then with alcohol and ether. Dry for 30 minutes at 338 degrees F. Weigh as peroxide of lead ( $\text{PbO}_2$ ) and for convenience calculate to litharge ( $\text{PbO}$ ), using the factor 0.933. No metals present in rubber mixings will interfere with this determination.

*Zinc.*—Wash the solution and the insoluble matter from the electrolytic beaker, from which the lead has been removed, into a litre beaker. Add five c.c. of concentrated sulphuric acid, evaporate dry, and drive off most of the sulphuric acid. This is done to insure complete removal of nitric acid, which would interfere with the electro deposition of zinc. After evaporation, cool and digest residue, which usually contains considerable insoluble, with 50-75 c.c. water. The zinc is now present as zinc sulphate and is readily soluble. Filter and wash. If the zinc oxide content is known to be low use entire filtrate, but if 20

per cent. or over, catch filtrate in 200 c.c. volumetric flask. Make up to mark and take 50 c.c.

Wash this portion of solution representing 0.25 grams of rubber sample into a 200 c.c. electrolytic beaker. Add considerable excess of saturated solution of sodium hydroxide over that necessary to redissolve the zinc hydroxide. Electrolyze at ordinary temperature at 2 to 2.5 amperes, rotating the anode for 20 minutes. Remove and wash with water, alcohol and ether. Dry at 212 degrees F. for a few minutes, cool and weigh.

Zinc is deposited on the cathode and is weighed as metal. The weight of zinc is calculated to zinc oxide. Aluminum will not interfere even if the solution is gelatinous from the precipitated aluminum hydroxide. In event that iron is present, filter off the iron hydroxide after adding just enough sodium hydroxide solution to insure solution of the zinc hydroxide. Then add further sodium hydroxide solution to this filtrate. Lead peroxide and zinc can be dissolved from the platinum gauze by concentrated nitric acid saturated with tartaric acid.

#### JOINT RUBBER INSULATION COMMITTEE'S SPECIFICATION FOR 30 PER CENT. *HEVEA* RUBBER COMPOUND.

(CHEMICAL CLAUSES.)<sup>9</sup>

1. A 30 per cent. fine Para or best quality plantation *Hevea* rubber compound with mineral fillers shall be furnished. It shall contain only the following ingredients: (1) rubber; (2) sulphur; (3) inorganic mineral matter; (4) refined oil paraffin or ceresin.

2. The vulcanized compound shall conform to the following requirements, when tested by the procedure of the Joint Rubber Insulation Committee, results being expressed as percentages by weight of the whole sample.

#### REQUIREMENTS INDEPENDENT OF THE AMOUNT OF RUBBER FOUND.

	Maximum	Minimum
Rubber .....	33	30
Waxy hydrocarbons .....	4	..
Free sulphur .....	0.7	..

Red lead, carbon, or organic fillers shall not be present.

<sup>9</sup> Joint Rubber Insulation Committee Report in "The Journal of Industrial and Chemical Engineering" (March, 1917). The procedure is outlined elsewhere in this chapter.

REQUIREMENTS DEPENDENT UPON AMOUNT OF  
RUBBER FOUND.

(Requirements for intermediate percentages shall be in proportion to the percentage of rubber found.)

	30 Per Cent. Rubber Compound		33 Per Cent. Rubber Compound	
	Maximum	Minimum	Maximum	Minimum
Saponifiable acetone extract..	1.35	0.55	1.50	0.60
Unsaponifiable resins .....	0.45	....	0.50	....
Chloroform extract .....	0.90	....	1.00	....
Alcoholic potash extract .....	0.55	....	0.60	....
Total sulphur (Note 2).....	2.10	....	2.30	....
Specific gravity .....	....	1.75	....	1.67

3. The acetone solution shall not fluoresce.

4. The acetone extract (60 c.c.) shall be not darker than a light straw color.

5. Hydrocarbons shall be solid, waxy and not darker than a light brown.

6. Chloroform extract (60 c.c.) shall be not darker than a straw color.

7. Failure to meet any requirement of this specification will be considered sufficient cause for rejection.

8. Contamination of the compound, such as by the use of impregnated tapes, will not excuse the manufacturer from conforming to this specification.

Note 1. This specification shall be supplemented by appropriate clauses relating to tensile strength, elasticity, electric insulation resistance and dielectric strength. (See the Wire and Cable Specifications of the American Society for Testing Materials, the Association of Railway Electrical Engineers, etc., for examples of such clauses.)

Note 2. The limit on total sulphur may be omitted at the option of the purchaser.

Experience has shown that compounds of the grade which contain only good *Hevea* rubber, may be relied upon to be more permanent than those made of rubber of other grades. It is not affirmed by the committee that a compound which conforms with this specification is necessarily permanent, or that a better compound cannot be made, but it is believed that enforcement of the specification will limit the use of inferior materials and that it will put the manufacturers more nearly upon equality of endeavor, where they can use their experience to obtain the best

results. Used in connection with the analytic procedure, the specification will enable purchasers to order a good compound and to ascertain, with a greater certainty than heretofore, whether the material received represents the compound specified.

The term *Hevea* applied to rubber means rubber from the *Hevea Brasiliensis* tree, whether wild or cultivated and regardless of the locality in which it has been grown. Para rubber is *Hevea* rubber of the kind originally shipped from the port of Para, Brazil, and comes in several grades. The rubber required by this specification should be *Hevea* rubber of good quality, such as fine Para or best quality plantation rubber.

Carbon is excluded, not only because it is considered, by some purchasers, to be deleterious, but because it interferes with the determination of rubber hydrocarbons.

Red lead is excluded because of the possibilities of its deleterious effects on rubber.

Ozocerite is prohibited because the acetone extract obtainable from it interferes with the separation of the acetone extract obtainable from the rubber, thereby vitiating the assay of the rubber extract. This prohibition is unimportant to the manufacturers, as ceresin, which is permitted, is the essential constituent of ozocerite.

An upper limit is placed upon the rubber in order to prevent the attainment of electrical and mechanical strength by the use of an extra quantity of inferior rubber whose lasting qualities might not be satisfactory.

The hydrocarbons are limited, owing to their tendency to separate from the compound and thus cause porosity.

The free sulphur is limited because an excessive amount may be deleterious.

The maximum limit on the saponifiable acetone extract is to prevent the use of raw or reclaimed rubber with high saponifiable extract. The medium limit assists in forcing the use of *Hevea* rubber, since it is characteristic of the acetone extract from *Hevea* to be largely saponifiable.

The unsaponifiable resins are limited because a low proportion of unsaponifiable resins is characteristic of *Hevea* rubber. A high result might be due to the presence of reclaimed rubber.



The chloroform extract is limited; first, to prevent the use of bituminous substances, and, second, to limit depolymerized and under-cured rubber.

The alcoholic potash extract is limited to prevent the use of saponifiable rubber substitutes.

The specific gravity is limited to reconcile the specification of ingredients by weight with the practice of purchasing material by volume.

Fluorescence of the acetone solution is prohibited, as it indicates the presence of bituminous substances, rosin oil or mineral oils.

The color of the acetone extracts is specified to conform with the normal color of the extracts of *Hevea* rubber. A darker color indicates adulteration or an inferior grade of rubber.

The hydrocarbons are required to be solid in order to prevent the use of oils and paraffin of low-melting point. The shade required is that obtained from paraffin wax or ceresin. Liquid hydrocarbons indicate reclaimed rubber softened with mineral oil, or paraffin of low-melting point.

The color of the chloroform extract is specified to conform with the color of dissolved gum in small quantities. The presence of bituminous substances would be indicated by a brown or black color.

It would be desirable that the sulphur of vulcanization be limited to exclude reclaimed rubber, which contains the sulphur of its previous vulcanization, but the committee has not yet developed an acceptable method for determining this quantity. It is, therefore, confronted with the choice of either placing a limit on the total sulphur or giving up the attempt to exclude shoddy by sulphur limitation. Option is, therefore, given to the purchaser to insert or omit the limit on total sulphur. Such insertion will at times exclude reclaimed rubber and the committee believes it possible to make a suitable compound with this limitation. The committee thinks that a sulphur limit positively excluding reclaimed rubber, would place too great a hardship, in other ways, on the manufacturers. Where the specification is used with no total sulphur limit, the use of many kinds of, or much reclaimed rubber,

will be guarded against by the limits of the various components of the acetone extract. When the limitation on total sulphur is omitted, sulphur-bearing fillers, which possess certain advantages, may be used.

This specification should be supplemented by appropriate elasticity and tensile strength tests, in order to add to the assurance that good rubber has been used and that the vulcanization process has been properly carried out; also by appropriate electric stress and resistance tests, to assure proper insulating qualities and homogeneity of structure. The exact value of the limits for these tests will depend upon the use to which the material is to be put.

The Joint Rubber Insulation Committee's chemical clauses, or analytical procedure for insulation, have been adopted by the following:

American Electric Railway (Engineering) Association: Standard Specification for Rubber Insulated Wire and Cable.

America Society for Testing Materials: Proposed Specifications for Insulated Wire and Cable; 30 per cent. *Hevea* Rubber.

Association of Railway Electrical Engineers: Standard Specifications for Wire and Cable.

Interborough Rapid Transit Co., Motive Power Department, New York: Specification No. 2.

New York Central Railroad Co., Electrical Department: Specification No. 300.

Panama Canal: Office of General Purchasing Agent, Circular No. 1,038.

Signal Corps, U. S. Army: General Specification No. 581-A.

#### PHYSICAL TESTING OF RUBBER GOODS.

THERE is a great variety of special appliances that afford really valuable tests as to the durability, tensile strength and wearing quality of certain kinds of goods. As a rule, these aim to subject the vulcanized article to conditions equivalent to those to which it will be subjected in actual service. For rubber boots and shoes, for example, a machine is employed which bends the shoe exactly as it is bent when the wearer is walking, and at the same time gives a friction motion on

the sole. This is run at high speed, so that a week's wear on the machine corresponds to a month of service in actual use.

A machine is also used for testing air-brake hose which counterfeits the swing and kinking motion that the hose gets in actual service. The hose which stands this sort of usage longest is supposed to be adapted to endure the longest time in actual use.

Tires, both pneumatic and solid, are tested by being put on a wheel rim and run the equivalent of hundreds and thousands of miles over roughened surfaces upon which they are pressed by a lever carrying heavy weight. These mechanical contrivances are valuable in showing the severe usage that rubber will often stand, but none of them are exact parallels to absolute service, for as a rule they are more severe, particularly in the intense heating that may come to the rubber from high speeds and great friction.

Manufacturers and purchasers of rubber goods have also many simple and excellent tests for approximating the value of the rubber. In belt and hose covers and tubes, a strip of the rubber is removed from the fabric and stretched to show its tensile strength. The fabric is also pulled apart, and the integrity of the friction proved by the way it resists such separation. Rubber springs sometimes have been placed under a steam hammer, which was allowed to drop upon them, the results being noted and that compound standing up longest being considered the best.

#### STANDARD METHODS FOR PHYSICAL TESTING.

The following methods are standard for the physical examination of vulcanized rubber goods as specified by the Board of Estimate and Apportionment of New York City:

**SAMPLING.**—The contracting department shall select and take all samples for testing. The number of samples and the quantity to be taken from the deliveries will depend upon the size of the articles and the quantity delivered.

Samples shall fairly represent the delivery, and pieces shall be taken from not less than one per cent. of the number of units delivered.

**AVERAGES.**—The results of tensile strength, elongation and set tests as reported, shall be the average obtained from the

samples received by the laboratory. Not less than three test pieces from each sample shall be tested and their results taken in calculating the average unless some individual result is apparently in error, in which case a retest shall be made.

TEMPERATURE OF TESTING ROOM.—Physical tests of rubber shall be made with the temperature of the air not lower than 65 or higher than 90 degrees F.

TIME.—All measurements of time shall be taken with an accurate stop watch.

#### PREPARATION OF TEST PIECES.

Test pieces of rubber shall be stamped out with a die, whenever practicable to do so.

TENSILE STRENGTH, ELONGATION AND SET TEST PIECES.—Test pieces of rubber for tensile strength, elongation and set tests shall be cut out with a die, either of the constricted bar or ring type. The same test piece shall be used for making all three tests. When the bar-test piece is prepared a die should be used that will make the constricted part of such a width that the cross section will be approximately one thirty-second of a square inch.

All pieces for these tests shall have the backing entirely removed, and any corrugations or irregularities of any kind shall be accurately buffed off, to make a uniformly smooth surface.

Test pieces which have become burnt in buffing shall be discarded.

Test pieces shall be kept constantly wet during the buffing.

Test pieces of rubber valves and odd-shaped rubber articles shall, whenever possible, be cut down on a lathe to an even thickness of not more than one-eighth inch and then cut out to shape for testing with a die.

If it is necessary to use naphtha to remove the backing or to separate the rubber from the plies, the naphtha shall be what is technically known as 76-degree Baumé, free from oil.

When naphtha has been used the test pieces shall be allowed to remain at rest for not less than one hour before testing.

In all cases where backing is removed and buffing done, the test pieces shall remain at rest for not less than ten minutes before testing.

**FRICTION TEST PIECES.**—Test pieces for friction or adhesion tests shall be cut and prepared as follows:

All kinds of hose, round packing and similar articles shall be cut transversely unless the diameter is so small that a practical measurement cannot be taken, in which case the test pieces shall be cut longitudinally.

Belting, packing or gasket material may be cut in any direction.

Test pieces from washers, ferrules (sleeves), molded gaskets and other odd-shaped articles shall be prepared in the manner called for in the unit specification, if it is impracticable to prepare them in accordance with these rules.

Cotton rubber-lined hose test pieces and braided hose test pieces shall be accurately cut transversely two inches wide and full length of the circumference. They shall be cut through the walls so that they can be laid out flat the full length of the piece. One-quarter inch of the rubber lining shall be carefully and cleanly trimmed off on each side, without injuring the fabric, leaving a strip of rubber lining one and one-half inches wide undisturbed on a strip of cover two inches wide. A separation between lining and cover of this strip shall be started for about one and one-half inches.

Test pieces of wrapped hose, round packing and similar articles shall be accurately cut transversely one inch wide and left circular, to permit sliding on to a mandrel. A separation between the rubber and the fabric or between the layers in accordance with the test to be made shall be started full width of the piece and far enough distant to permit proper fastening of clamps or hooks, as the case may be.

Solid round packing and similar articles shall have a core drilled out for the mandrel.

Fabric-backed rubber packing test pieces shall be prepared in the same manner as for cotton rubber-lined hose, except that if the rubber part is more than one-eighth inch thick, the test piece shall be prepared exactly opposite, leaving a strip of sheeting one and one-half inches wide on a strip of rubber two inches



wide. A separation between sheeting and rubber shall be started for about one and one-half inches.

Belting test pieces shall be accurately cut one inch wide and shall be stripped down to all but two plies, and a separation of the two plies started for about one and one-half inches.

All pieces of flat material, such as packing, gasket, belting, etc., shall be cut not less than 12 inches long whenever possible.

#### DETERMINATION OF TENSILE STRENGTH.

The determination of tensile strength of the rubber compound shall be made as follows:

APPARATUS.—All tensile strength tests shall be made on an apparatus the general design of which conforms to the Schopper machine.

GRIPS.—When bar-test pieces are used, the grips for holding the test pieces shall be such that they will tighten automatically, exerting a uniform pressure proportionate to the applied tension across the full width of the piece, regardless of any variation in the thickness of the rubber.

RING-TEST PIECES.—These shall be placed over the revolving rollers of the Schopper machine.

MARKING BAR-TEST PIECES.—The bar-test pieces shall be stamped in center portion with two lines two inches apart, using a rubber ink-pad stamp. The distance between the outside edges of these stamped lines shall be accurate to one one-hundredth of an inch.

MEASUREMENT OF BAR-TEST PIECES.—The width and thickness of the test pieces shall be accurately determined at three points equidistant between the marks, a spring gage or ratchet stop micrometer being used.

MEASUREMENT OF RING-TEST PIECES.—The width and thickness of the test ring shall be accurately determined at not less than four opposite points on the ring, care being taken to get the minimum cross section as near as possible, the area of which shall be used in computing the tensile strength.

BREAKING.—Bar-test pieces shall be tightly fastened in the jaws and brought just taut. The machine shall then be started and the speed so regulated throughout the entire test that the jaws separate at the uniform rate of 20 inches per minute.

The number of pounds necessary to break the test piece shall be read to the nearest tenth of a pound and computed to pounds per square inch, using the measurements nearest to the break.

When breaking the ring-test piece the ring shall be slipped over the revolving bearing provided for it and the procedure continued exactly as for the bar-test piece, the speed being so regulated that it will give an equivalent elongation of test piece per minute.

#### TENSILE STRENGTH ACROSS THE SEAM.

Bar- and ring-test pieces shall be prepared as usual, except that the seam shall not be buffed off.

In cutting, the seam shall be centered in the middle of the bar-test piece, at right angles to the axis, as nearly as possible.

The center of the seam shall be made to lie along a diameter of the ring-test piece as nearly as possible.

The calculation shall be based on the average cross section in both kinds of test pieces in the usual manner, but excluding the cross section of the seam or seams.

#### ELONGATION AT THE BREAKING POINT.

The elongation at the breaking point shall be accurately determined during the tensile strength test as follows:

On the bar test a rule graduated to hundredths of an inch shall be kept opposite the two marks and the distance the outside edges of these two marks are apart at the instant of breaking shall be noted.

This distance shall be computed into per cent. of elongation; i. e., if the marks are twelve inches apart at the break, that piece would have 500 per cent. elongation.

**RING-TEST PIECES.**—These shall have the elongation read to the nearest whole per cent. from the automatic record on the stretch tapes.

#### DETERMINATION OF SET.

The determination of set shall be on the test piece as broken in the tensile strength test not less than one nor more than one and one-half minutes after breaking. Time shall be taken with a stop watch.

BAR-TEST PIECES shall have the distance from the outside of the line to the furthest broken point measured carefully along the axis on one broken portion to the nearest one-hundredth inch and in the same manner from the corresponding nearest broken point on the other portion. The sum of these two measurements, minus two inches, is the actual set, and shall be computed to percentage of the elongation at rupture to the nearest tenth per cent.

RING-TEST PIECES shall have the inner circumference carefully measured around a solid disk of the same diameter as the inside diameter of the original ring. The increase in length (actual set) is read to the nearest half per cent., divided by the per cent. elongation at rupture, and the result recorded to the nearest tenth per cent.

#### DEFECTS.

If the break occurs outside the gage marks on the bar-test piece during the tensile strength test, the specimen shall be considered as defective for any determination, and another test made.

The broken surfaces of both test bars and test rings shall be examined for flaws or defects, and if the results of the tests confirm the observation of flaws the test pieces shall be replaced by others.

#### PHYSICAL PROPERTIES AND TESTS OF AIR BRAKE AND SIGNAL HOSE.<sup>10</sup>

Hose shall be subjected to the following tests, which must be made at a room temperature of not less than 65 degrees F.

TEST SPECIMEN.—A hose shall be selected at random and a section five inches cut from one end. Two sections, each one inch long, shall be cut from the 5-inch section for making friction, stretching and tensile tests; the remaining three-inch section shall be used for making additional tests, which may be desired on the tube and cover. Stretching and tensile test specimens shall be cut from the tube and cover with a die to standard dimensions specified.

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<sup>10</sup> From Master Car Builders Association Standard Specifications, 1915.

**FRICTION TEST.**—The quality of friction shall be determined by suspending a 20-pound weight from the separated end of the duck of one of the 1-inch test specimens previously described, the force being applied radially. The separation shall be uniform and regular, and the average speed shall not exceed 8 inches in 10 minutes, the distance being measured while the weight is still in place.

**STRETCHING TEST.**—Test specimens from tube and cover will be quickly stretched until the 2-inch marks are 10 inches apart and immediately released. They will then be re-marked as at first within 10 seconds after starting to release and again stretched to 10 inches between the new marks, remaining so stretched for 10 minutes. The specimens shall then be completely released, and within 30 seconds after starting to release the distance between the marks last applied will be measured, and the initial set must not be more than  $\frac{1}{4}$  inch. At the end of 10 minutes the distance between the marks will again be measured, and the final set must not be more than  $\frac{1}{8}$  inch. These test specimens may be cut from the tube and cover of the friction-test specimen, but shall not be used for tensile test.

**TENSILE STRENGTH.**—Test specimens from tube and cover shall be pulled in a tensile machine with a test speed of 20 inches per minute. The inner tube must have a tensile strength of not less than 800 pounds or more than 1,200 pounds per square inch, and the cover not less than 700 pounds or more than 1,100 pounds per square inch. The elongation shall be such that the marks, originally two inches apart, stretch to at least 10 inches before specimen breaks. If the tensile strength in pounds per square inches is greater than that required, the sample may be accepted, providing the per cent. increase in elongation is equal to or greater than the per cent. increase in tensile strength in pounds per square inch above the maximum figure.

**POROSITY TEST.**—The remaining 17 inches shall be mounted and placed in a test rack; the circumference will be measured and the hose filled with air at 140 pounds pressure per square inch; the rubber cover shall be cut from clamp

to clamp (taking care not to injure the duck) and this pressure maintained for five minutes. At the end of this time the hose will be submerged in water to determine whether the inner tube is porous. The escape of air through the tube shall be distinct enough so that porosity will not be confused with the escape of air which is confined in the structure of the hose. In the event the hose fails on bursting test at the point at which cut was made for porosity test and a satisfactory hydraulic test is not obtained, the porosity and hydraulic test will be repeated on another piece of hose.

**BURSTING TESTS.**—The section of hose, which was used for porosity test, shall then be subjected to a hydraulic pressure of 200 pounds per square inch, under which pressure it shall not expand in circumference more than  $\frac{3}{4}$  inch for air-brake hose and  $\frac{1}{8}$  inch for air-signal hose, nor develop any small leaks or defects. After the above test, this section shall then stand a hydraulic pressure of 500 pounds per square inch for 10 minutes, without bursting or developing any small leaks or defects, after which the hydraulic pressure shall be increased to a minimum of 700 pounds per square inch without bursting, at the rate of not less than 100 or more than 200 pounds per five seconds.

#### RELATIONSHIP OF MECHANICAL TO CHEMICAL PROPERTIES.<sup>11</sup>

FROM experiments made there is no question that the combined sulphur at "optimum" cure in the case of *Hevea* plantation rubber is a remarkably constant quantity, equal on the average to approximately 2.8-3 per cent. Where more than this amount of combined sulphur has been found, either the method of vulcanization is at fault or the means of determining the "optimum" cure are inaccurate. In this connection it is necessary to point out that in the case of very soft, low-grade rubbers it is difficult to judge of the "optimum" cure, and there is always the tendency to increase the cure to beyond the "optimum" point in the hope of thereby improving the physical or tensile properties of the product. In the case of any good grade of *Hevea* plantation rubber there is no such

<sup>11</sup> Doctor D. Spence, "On the Relationship of Mechanical to Chemical Properties." "India Rubber Journal," December 9, 1916.



difficulty, however, and where more than 2.8-3 per cent. of combined sulphur is reported in this case, either the sample is over-cured, or what amounts to the same thing, vulcanization has not been properly carried out. With proper methods of vulcanization, and with the requisite experience in the judging of the proper cure, the combined sulphur at "optimum" cure should never greatly exceed the figures we have given. It should be pointed out, however, that if the time of cure required to produce the "optimum" result is extended, the chances are an increase in the amount of the combined sulphur at the "optimum" point over the figures we have given will be found. Depolymerization, requiring an increase in cure to bring the rubber up to apparent physical "optimum" leads to an increase in the combined sulphur considerably over the amount which we have given. The rubber in this case is, nevertheless, over-cured, and where the vulcanization of the rubber is carried out scientifically, in a minimum of time, and with the least possible injury to the molecule, the combined sulphur at "optimum" cure will never be found to exceed three per cent.

Whether these figures obtain for rubbers of different botanical origin or not we have not sufficient analytical evidence at present to say. The constancy of this result is deduced from experiments made on *Hevea Brasiliensis* rubber only. The relation between the rubber and combined sulphur at correct cure is so constant that it is regarded as representing a more or less definite compound of rubber and sulphur to which a formula may be assigned on the assumption that partial valencies of the rubber aggregate have not all the same affinity for sulphur.

It may be of interest to record the fact that we have observed that the point at which the physical properties of pure balata on vulcanization suddenly change to more nearly resemble those of rubber, corresponds very closely with a combined sulphur content of three per cent. If pure balata is mixed with a little sulphur and a suitable catalyst, which is essential to its proper vulcanization, it will be found that when about three per cent. of sulphur has combined with the balata, the physical properties of the vulcanized balata change

from those of a hard, inelastic product, more like hard rubber, to a pliant, semi-elastic product, more nearly resembling soft vulcanized india rubber. This phenomenon is exceedingly remarkable and interesting, as the transition point in the physical characteristics of balata on vulcanization occurs at about the same degree of chemical vulcanization as corresponds to the "optimum" cure of vulcanized india rubber. This has given rise to a number of experiments by us, with a view to converting balata into rubber and vice versa, some of which have led to exceedingly interesting results.

#### COEFFICIENT OF VULCANIZATION AND THE STATE OF CURE.

HENRY P. STEVENS states<sup>12</sup> that if physical tests on vulcanized rubber are to be of practical value in deciding the manufacturing value of any particular specimen, these tests must be carried out on a rubber cured suitably to meet manufacturing conditions; or, if on a rubber cured beyond this stage (over cured), there must be available some method by which the tests on the over-cured rubber may be correlated to tests on correctly cured rubber. No such method of calculation is at present available, as the necessary relationship has not been worked out between stress-strain curves and coefficient of vulcanization. A correctly cured rubber is one fully cured from the manufacturer's standpoint, not beyond that point at which aging is satisfactory. Otherwise the specimen is over-cured.

Rubber is a colloid, and shows the phenomena of hysteresis. Its physical properties at any moment depend partly on its previous history. It is therefore obvious that no conclusions should be drawn from any stress-strain curve without taking into consideration the previous history of the specimen. Dr. Stevens agrees with the statement of Dr. de Vries that "the percentage of combined sulphur is quite independent of the state of cure *as expressed* by the position of the stress-strain curve," but adds that the "state of cure" cannot be adequately expressed under present conditions by the stress-strain curve. It may, however, be possible when the "stand-

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<sup>12</sup> "India Rubber Journal," February 10, 1917.

ard curve" or other methods are correlated to manufacturing conditions and the tests carried out on rigidly standardized lines.

Vulcanization is essentially a chemical process; so also is the subsequent decomposition of rubber which has been over-cured, and hence the proportional relationship of rubber and sulphur in combination is the best guide for a stable product, the first essential in the manufacture of rubber goods.

Discussing the case in which the "coefficient" (according to Stevens) may be wrong, but the mechanical properties correct, Schidrowitz and Goldsborough note that the question at issue is whether state of cure or correct cure is to be judged by the chemical or the mechanical properties of the vulcanized article—by sulphur combined with the rubber or by the stress-strain curve. Their answer is that *ultimately* the attributes or quality of vulcanized rubber must be judged by the physical or mechanical properties.

Certain low-curing rubbers require, in order to acquire the necessary mechanical properties, a protracted cure, and in the course of such cure will combine with more than three per cent. of sulphur, and in general slow-curing rubbers deteriorate more rapidly than rapid-curing goods, and will not age well because of the excess of combined sulphur, and possibly also by reason of the long heating necessary.

The physical and mechanical effects which vulcanization has upon rubber are shown in the clearest manner by the stress-strain curve method, and there is no other known method whereby the mechanical aspect of vulcanization can be systematically and accurately followed and measured.

Regarding this method, its authors, Schidrowitz and Goldsborough remark:

In view of the apparent lack of comprehension concerning stress-strain curves, we take this opportunity of briefly re-stating some of the more important points.

1. The "type" of the curve is *independent of the state of cure*. It therefore connotes inherent properties.

2. As the "type" varies for different rubbers, its determination affords a valuable method of comparison in regard to important mechanical properties.

3. We obtain a graphic representation of the progress of vulcanization.

4. We are able to cure to a definite mechanical condition, and to estimate the rate of cure necessary to attain that condition.

5. Having settled the position of the curve for a given rubber mixing we are able to control the vulcanization of the factory product.

Much else may be done with and deducted from the stress-strain curve method. In more propitious times the authors propose to recur to the subject at length.

While agreeing that stress-strain curves are of great value, intelligently applied, Dr. Stevens holds that the coefficient of vulcanization is the safest guide as to the state of cure.

#### SPECIFIC GRAVITY IN RUBBER COMPOUNDING.

The relation of bulk to weight depends on the specific gravity of the material and is of great importance in the rubber industry because it controls the number of pieces per pound in molded rubber goods, and the rubber-coated area obtainable per pound in the case of coated fabrics, from any given stock.

The specific gravity of any substance is the particular ratio of its weight to that of an equal bulk of another substance taken as standard, or unit weight. For all solids and liquids, the standard substance of unit gravity is distilled water at 62 degrees F. For gases the standard is hydrogen gas at the atmospheric pressure of the sea level.

The method of determining specific gravities of solids depends on the fact that any insoluble substance immersed in water loses weight equal to the weight of the volume of water which it displaces. The means of ascertaining specific gravities vary according as the substance under examination is solid, liquid, or gaseous.

In the case of solid bodies, not in powdered form, a balance or other weighing apparatus is employed by which the weight of the material in air and its loss of weight in water may be determined. These values having been found experimentally, the specific gravity is ascertained by dividing the weight of the material in air by its loss of weight in water. For rapid determinations of specific gravity, special instru-

ments are often used; for example the spiral balance, or a direct reading instrument, known as a gravitometer.

For materials in the form of powder the specific gravity bottle is used. This is of various forms, but is essentially a small glass-stoppered flask provided with a reference mark on the neck. A fine chemical balance is necessary to make the weights and the procedure is as follows<sup>13</sup>, for solids heavier than water:

Weigh the flask filled to the mark with water, then place the substance, of known weight, in the flask, fill to the mark with water, and weigh again. The calculation of the specific gravity will be:

$$\text{Specific gravity} = \frac{(\text{Weight of substance in air}) + (\text{weight of flask and water}) - (\text{weight of flask and water and substance})}{(\text{Weight of substance in air})}$$

It should be noted that specific gravity is not to be taken as a test for quality as applied to rubber compounds, but should be considered simply as a factor in the economy of any given stock. A practical application is found in estimating the weight of a proposed article when its net cubical contents of stock is known. The weight for water of the cubical contents is ascertained by multiplying by 252.5, the weight in grains of one cubic inch of water. This product, multiplied by the specific gravity of any material, will give the weight of the object in that material.

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<sup>13</sup> From Bailey's "Chemists' Pocket Book."



## CHAPTER XIX.

### PRIMARY PROCESSES, DIVISIONS OF RUBBER MANUFACTURE AND TYPICAL COMPOUNDS.

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#### WASHING, DRYING, MILLING, CALENDERING, AND SPREADING.

THE very first manufacturing process in the manipulation of rubber of any kind, and for any use, is that of cleansing. This is usually done by passing the gum repeatedly between corrugated rolls, while fine streams of water remove the various impurities that are exposed by the tearing action of the rolls. These impurities are bits of vegetable substances, earth, sand, etc. The old type of washer for removing these was a couple of corrugated rolls 6 or 8 inches in diameter, and 12 or 14 inches in length. Modern methods, however, have introduced larger rolls, until today one machine, when it is the highest type of three-roll washer, will cleanse enough gum to keep a huge factory busy.

There are also a number of enclosed washers of the masticator type that do excellent work and for some purposes are preferred to either the open roll or the hollander type of machine.

Some rubbers are so full of sand that it is almost impossible to remove it wholly. For this purpose is used a tub with a false bottom made of fine wire, and also with a stirrer. "Thimbles," for instance, after being run through the washer, are put in the tub without any attempt at sheeting, and stirred until a large portion of the sand is removed.

Another type of washer is one that is quite similar to a paper engine; in fact, paper engines are often used in rubber washing. The special value of this type is that the rubber in its movement about the tub is floated more or less, and the sand and earthy matters sink to the bottom, while the bark and vegetable matters can be seen and easily removed.

Some manufacturers, following Austin G. Day's ideas, have used alkaline solutions in washing certain gums, to neutralize the vegetable acids, and it is a question if it might not be as well to use dilute acids to neutralize the strong alkaline qualities of gums that go through certain kinds of coagulation. Some factories also examine the coarser grades of gums, chemically, and give them a treatment to remove odor. As a rule, however, manufacturers rush them through the washing machines, sheet and dry them, and get them into the mixing mills as soon as possible.

**DRYING.**—The drying of rubber, according to earlier practice, required a great deal of time. It was the boast of more than one rubber mill that no Para rubber was used by them until it had been dried for a year. The manufacturers of mechanical rubber goods were the first to break away from this tradition. In many cases they found, when there were rush orders on hand, that they must put on their mills gum that was practically just off the washer, and mix it, or else lose orders. Of course, they were forced to get most of the moisture out, or neutralize what was left, and they learned incidentally that they got a stronger compound with the green gum than with the "seasoned," whence the belief grew up that the months and years of drying were not necessary, as had before been supposed. In addition to this, some of them learned that long drying meant oxidation on the outside, or the turning of rubber into resin, which further increased their doubt of the wisdom of the slow-drying process.

These thoughts once entertained, it was not long before various plans were introduced into the drying, for hastening the removal of the moisture. The simplest of these, of course, was artificial heat, and the presence of a fan for removing the moisture-laden atmosphere. Later developments have brought about a process, lasting only a few hours, for drying rubber very cheaply at quite a high heat, thereby giving it hot from the dryer to the man who runs the mixer, and doing away with the expensive process of breaking down. This latter idea is to some, of course, as revolutionary as was the first thought of quick drying, but that it is wholly in the line of progress is proved by the fact that it has now been used for a number of years by many manufacturers whose goods stand very high.

**MILLING.**—The milling of crude rubber is simply putting on hot rolls the dry rubber which is found in a tough, intractable sheet, and running it until it gets to be a softened, homogeneous mass. The gum, when this is accomplished, is ready for mixing. These mixing rolls are run at different speeds and are called friction rolls, and the various adulterants and ingredients that are to be incorporated with the rubber are pressed into the softened gum by their revolution.

No general rule can be laid down for mixing in all lines. An expert compounder knows that certain gums should be mixed on cool rolls, and others under considerable heat. His knowledge of specific compounds teaches him to hasten mixing in many cases, where another, without skill, would require very much more time to get the same result. In some cases the ingredients are put in together, in others it is necessary to add them in definite order. Some have dissolved substances that would make the rubber stick to the rolls like glue unless they were put in at just the right time; others have so large a proportion of earthy matters that, unless the gum be humored, it apparently will not take them in, and so on. Each line of work and, in fact, each factory has its own special methods, and often one or more skilled mixers who can handle compounds that none of the others seem to be able to do anything with.

**CALENDERING.**—The use of the calender is to sheet the goods so that they may be easily made into the desired forms. The simplest form of calender is a mixing mill with the key withdrawn that normally holds one roll in place, so that both run by even motion. This is used in many small factories where nothing but molded work is made.

The modern sheeting calender is ordinarily a three-roll machine. It is sometimes made with four or more rolls, however, and these rolls may be almost any size, the widest for rubber work being more than 80 inches. A considerable degree of skill is required for running the calender on a variety of stocks, nor can any general rules be laid down for calender work. This is proved by the value that is set upon good calender men, and by the difference that there is between the work of a good one and a poor one. There are as many different kinds of calenders as there are patterns of mixing mills. A sheet calender

has smooth rolls, and is for running absolutely smooth goods. In shoe work there are engraved rolls, pebbled rolls, and soling calenders engraved with knurled surface to produce the rough shoe sole. The carriage drill business has embossing calenders, and so on. A type of calender that is useful in most lines of work is known as the friction calender, the rolls in which run at uneven speeds and drive the gum deeply into or through the meshes of the fabric.

SPREADING.—Where india rubber is handled in solution there is used in place of the calender a spreading machine, known under the various names of "Yankee flyer," "English spreader," "doughing machine," etc. In this a sheet of rubber is spread on the cloth by being placed on an endless apron of the fabric, the apron running over the roll, against which hangs a heavy knife. A very thin coating of the rubber solution is constantly scraped off this surface, which then passes over hot drums or steam chests, evaporating the solvent.

#### DIVISIONS OF RUBBER MANUFACTURE AND TYPICAL COMPOUNDS.

THE foremost European manufacturers of rubber goods, as a rule, make everything in the line of compounded rubber, hard or soft, and in addition often are producers of gutta-percha goods. In the United States, on the other hand, the tendency has been to specialize, and as a result the industry has divided itself naturally into the following general lines: mechanical rubber goods; tires, pneumatic and solid; molded work; sundries, druggists', surgical, and stationers'; dental and stamp rubbers; surface clothing; carriage cloth; mackintoshes and proofing; boots and shoes; insulated wire; hard rubber; cements; notions; plasters; and reclaimed rubber.

The following brief description of the manipulation of rubber in these various lines is given because there are superintendents and managers who are experts in one line but who may be wholly unfamiliar with machinery and processes used in other lines.

#### MECHANICAL RUBBER GOODS.

This line of rubber manufacture, which is also known in Europe as technical rubber goods, embraces all the heavier com-

binations of india rubber, metal, and fabric which are used in engineering and industrial lines. It covers, for example, belting, packings, hose, and special articles of almost endless variety and description.

This portion of the rubber business has always been the pioneer in the production of new compounds, new processes, and better and heavier machinery. Its manufacturers always have welcomed new grades of rubber, have been the first to utilize those that were a drug on the market because of lack of knowledge as to their manipulation, were familiar with the uses of reclaimed rubber while yet other lines were simply considering its use, and with hundreds of compounds and cures and a broad knowledge of industrial achievement in all lines, they have often pointed the way for manufacturers in other lines to follow, to the betterment of their goods or their pockets.

The mechanical rubber goods factory has the same general outfit in the way of machines for manipulating the crude gum as have the other lines. Their mixing mills, however, are often heavier, and their calenders run at higher speeds, while they have, in addition, enormously heavy hydraulic belt presses, huge vulcanizers, and scores of special machines designed for individual problems required for their line of work, or perhaps for a single factory alone. The kinds of vulcanization used in this work are (1) open steam heat, where the goods are buried in talc or wrapped in fabric; (2) dry heat, where they are confined by molds, and held in a steam press during the cure; or (3) where the goods, as in the case of belts, are molded between the platens of the press itself, while curing. Even in this line of work there are some concerns that do only special parts of it. For example, there are factories that make only certain types of packings which have a world-wide sale, and on which they are run continuously.

## COMPOUNDS FOR MECHANICAL GOODS.

FRICTION FOR BELTING.		COVER FOR BELTING.	
Central American .....	27.5	Coarse Para .....	20.00
African small balls .....	12.0	Best shoe reclaim .....	45.00
Barytes .....	16.0	White substitute .....	12.50
Litharge .....	23.5	Barytes .....	12.50
Whiting .....	13.0	Litharge .....	4.00
Sulphur .....	8.0	Whiting .....	4.00
		Sulphur .....	2.00



## COMPOUNDS FOR MECHANICAL GOODS.—(Continued)

## CHEAP WATER HOSE COVER.

Coarse Para .....	12.50
Best shoe reclaim .....	50.00
White substitute .....	7.00
Barytes .....	15.00
Litharge .....	2.50
Fine rags .....	10.00
Sulphur .....	1.25
Cotton seed oil .....	1.75

## CHEAP WATER HOSE LINING.

Coarse Para .....	5.5
Assam .....	5.5
African .....	5.5
Best shoe reclaim .....	32.5
White substitute .....	5.0
Zinc oxide .....	8.0
Barytes .....	8.0
Litharge .....	8.0
Whiting .....	8.0
Blue lead .....	8.0
Sulphur .....	3.0
Cotton seed oil .....	3.0

## PERFORATED MATS OR PACKING.

Coarse Para .....	7.75
Assam .....	5.75
Best shoe reclaim .....	29.00
White substitute .....	7.75
Black substitute .....	5.75
Zinc oxide .....	5.75
Barytes .....	13.50
Whiting .....	7.75
Sublimed lead .....	7.75
Litharge .....	5.75
Lime .....	0.50
Sulphur .....	2.00
Cotton seed oil .....	1.00

## MATTING.

Borneo .....	7.50
Shoe reclaim .....	44.50
Whiting .....	18.50
Sublimed lead .....	4.00
Litharge .....	7.50
Zinc oxide .....	9.00
Soapstone .....	7.00
Sulphur .....	2.00

## BILLIARD CUSHIONS.

Fine Para .....	50.00
Assam .....	21.00
Sublimed lead .....	7.00
Barytes .....	7.00
Litharge .....	3.50
Blue Lead .....	7.00
Sulphur .....	4.50

## FIBROUS GASKETS.

Fine Para .....	13.5
Coarse Para .....	13.5
Fine rags .....	13.5
Zinc oxide .....	13.5
Barytes .....	10.0
Litharge .....	5.0
Soapstone .....	14.0
Whiting .....	5.0
Sulphur .....	3.0
Blue lead .....	9.0

## RED SHEET PACKING.

Coarse Para .....	10.00
Pernambuco .....	10.00
Gambier .....	10.00
Red oxide .....	7.50
Asbestine .....	55.00
Sulphur .....	5.50
Lime .....	1.00
Coconut oil .....	1.00

## BLACK SHEET PACKING.

Lopori .....	22.0
Mechanical goods reclaim ..	22.0
Zinc oxide .....	17.0
Sublimed lead .....	15.0
Asbestine .....	7.0
Whiting .....	12.0
Lampblack .....	3.0
Lime .....	1.0
Sulphur .....	1.0

## MACHINE ROLL.

Fine Para .....	35.0
African tongues .....	14.0
Zinc oxide .....	14.0
Litharge .....	14.0
Paris white .....	18.0
Sulphur .....	3.5
Lampblack .....	1.0
Lime .....	0.5

## WRINGER ROLL, INSIDE.

African small ball .....	14.5
Pontianak .....	14.5
White vulcanized rubber dust	44.5
Cotton fiber .....	14.5
Sulphur .....	12.0

## WRINGER ROLL, OUTSIDE.

Coarse Para .....	18.00
Congo ball .....	7.00
Zinc oxide .....	31.00
Paris white .....	42.00
Sulphur .....	1.75
Lime .....	0.25

## WHITE TUBING, NO. I.

Fine Para .....	21.5
Coarse Para .....	21.5

COMPOUNDS FOR MECHANICAL GOODS.—(Continued)

WHITE TUBING, NO. I.—(Con.)

Zinc oxide .....	51.5
Sulphur .....	4.5
Lime .....	1.0

WHITE TUBING, NO. II.

Fine Para .....	21.50
Coarse Para .....	21.50
Zinc oxide .....	25.50
Whiting .....	20.00
White substitute .....	5.75
Sulphur .....	5.75

CHEAP WHITE TUBING.

Coarse Para .....	7.50
Mozambique .....	7.50
White substitute .....	9.00
Zinc oxide .....	45.00
Whiting .....	21.00
Sulphur .....	3.00
Lime .....	1.00
Palm oil .....	6.00

FIBER SOLE.

Fine Para .....	30.0
Reclaim .....	10.0
Mineral rubber .....	5.0
Cotton fiber .....	22.0

FIBER SOLE.—(Con.)

Lithopone .....	27.0
Calcined magnesia .....	3.0
Sulphur .....	3.0

WHITE SOLE.

Coarse Para .....	22.0
Ground waste rubber .....	43.5
Zinc oxide .....	11.0
Black substitute .....	11.0
Lime .....	6.5
Sulphur .....	6.0

RED SOLE.

Coarse Para .....	15.0
Red inner tube reclaim....	40.0
Ground red soling .....	12.0
Whiting .....	14.0
Red oxide of iron .....	10.0
Calcined magnesia .....	3.0
Sulphur .....	6.0

HEELS.

Coarse Para .....	10.0
Auto tire reclaim .....	36.0
Ground waste rubber .....	20.0
Mineral rubber .....	3.0
Litharge .....	2.0
Zinc oxide .....	15.0
Whiting .....	12.0
Sulphur .....	2.0

BOOTS AND SHOES.

The manufacture of rubber boots and shoes, although apparently a simple business, not only requires large capital, but is one that has often been overtaken by disaster. It is a matter of common knowledge that, given the same compounds, the same machinery, and the same skilled workmen, no two mills are able always to turn out exactly the same grades of goods. Quality is one ingredient that may or may not be added to the goods, no matter how honest the endeavor. That there are reasons for this, no one can doubt, and that the day will come when this branch of manufacture will be an exact science is probably true. That, however, will entail a definite knowledge of rubber from the moment it first sees the light as creamy liquid exuding from the tree, through every event in its life—in coagulation, transit, storage, factory manipulation, compounding, calendering, curing, its death in the service of man, and its later resurrection in the process of reclaiming. The need for exact information regarding the ingredients added in the course of compounding

and their relation to each other, mechanically and chemically, has been met by scientific study with marked improvement in quality of goods, machinery, and processes.

In the complete rubber shoe plant there are found, for initial equipment, washing rolls, mixers, refining mills, and calenders such as most of the other lines employ. In addition, there are special calenders, with engraved rolls for shoe-upper work; others, also, with engraved rolls for soling; presses for molding boot heels, sole-cutting machines, and, of course, vulcanizers. As this class of goods is cured by what is known as the "dry heat"—that is, by being confined in dry, hot air for several hours—it will readily be seen that it is a radically different business from mechanical rubber goods, for instance. These dry heaters are simply large, ventilated rooms, fitted with steam pipes for heating, lined with tin, double walled to prevent radiation, into which hundreds of pairs of boots or shoes are run on skeleton cars, to undergo the process of vulcanization. The manufacture of rubber footwear, in brief, therefore, consists in washing, drying, compounding and calendering the rubber and fabrics, the cutting of the calendered sheets into various shapes for cementing over lasts in the shapes desired, varnishing, and the dry-heat cure.

The usual method of curing rubber boots and shoes consists in exposing them on racks in large, dry heaters where the temperature of the air is slowly raised by steam circulating in coils beneath the racks. Moisture and volatile products escape by natural ventilation through openings in the roof of the heater. The air, a poor conductor of heat, circulates slowly and without pressure. The working conditions are therefore not under positive control, and the time of vulcanization is long, usually from eight to ten hours. The fact that the goods, during vulcanizing, are not under pressure permits the formation of blisters wherever included air or moisture is present. The loss from this cause is sometimes very considerable, and difficult to remedy. Other defects of the dry heater system of curing are irregularity of cure, due to faulty circulation of the air; excessive space required to handle the goods, because the cure is protracted unduly, and large cost of operation. Notwithstanding these defects and drawbacks, the dry heater has remained

the standard method for curing footwear since the earliest days of rubber manufacturing.

The rubber boot and shoe industry is indebted to Hon. A. O. Bourn, of Bristol, Rhode Island, for the introduction of the first practical process for the pressure cure of footwear, which he developed in his own works at Providence, Rhode Island. Since his invention several others have been perfected, the work chiefly of American manufacturers. These methods of pressure cure mark the most important recent advance in the boot and shoe branch of the rubber industry, because they bring under control and obviate many of the troubles and inconveniences inherent in the older process of curing footwear.

Manufacturers are now able, by these inventions, to control the vulcanizing process and produce better goods with fewer seconds. It is now possible to expel all air trapped between the plies in making, and under pressure to cure the shoe structure compactly together. Pressure cure, by direct steam, also allows the use of tough wearing and oil resisting mechanical stocks, such, for example, as automobile tire tread compound.

Other important advantages, due to these improved methods, are great economy of space formerly devoted to heaters, and a very important saving of time in vulcanizing. These points materially increase the curing capacity of a factory, while the effectiveness of the process not only produces better goods, but permits the manufacture of boots and shoes of any desired color. This matter of freedom in color selection is an important one from a trade viewpoint, adding markedly to the variety and attractiveness of the goods.

In the manufacture of mechanical goods the standard methods of cure have commonly been pressure methods by steam heat, applied either in an atmosphere of steam or by steam-heated molds. The patented processes of pressure cure for boots and shoes are adaptations of these means to the special conditions of footwear manufacture by evolving certain general methods for removing trapped air and curing the goods compactly.

These methods are in brief:

1. Consolidation of structure of the goods by pressure of air or non-oxidizing gases and the application of their heat or that of steam.

2. Removal by vacuum of entrapped air and vulcanization by pressure and heat applied by air, non-oxidizing, gases, or steam.

3. Compression of the goods by inflation or otherwise, in a mold heated internally or externally by steam, for vulcanization.

#### BOOT AND SHOE COMPOUNDS.

##### SHOE UPPERS, HIGH GRADE.

Fine Para .....	10.0
Coarse Para .....	18.0
Sulphur .....	1.0
Litharge .....	10.0
Lampblack .....	1.0
Coal tar .....	10.0
Whiting .....	50.0

##### SHOE UPPERS, MEDIUM GRADE.

Fine Para .....	5.0
Coarse Para .....	15.0
Shoe reclaim .....	10.0
Sulphur .....	1.0
Litharge .....	8.0
Lampblack .....	1.0
Coal tar .....	24.0
Whiting .....	36.0

##### BOOT UPPERS, HIGH GRADE.

Fine Para .....	30.0
Coarse Para .....	15.0
Sulphur .....	1.0
Litharge .....	15.0
Lampblack .....	2.0
Coal tar .....	10.0
Whiting .....	27.0

##### BOOT UPPERS, MEDIUM GRADE.

Fine Para .....	9.0
Coarse Para .....	25.0
Shoe reclaim .....	10.0
Sulphur .....	2.0
Litharge .....	10.0
Lampblack .....	2.0
Whiting .....	30.0
Coal tar .....	12.0

##### SHOE SOLING, HIGH GRADE.

Fine Para .....	10.0
Central American .....	12.0
Shoe reclaim .....	20.0
Sulphur .....	1.0
Litharge .....	10.0
Lampblack .....	1.0
Asphaltum .....	8.0
Whiting .....	38.0

##### SHOE SOLING, CHEAP GRADE.

Coarse Para .....	10.0
Shoe reclaim .....	46.0
Sulphur .....	1.0
Litharge .....	6.0

##### SHOE SOLING, CHEAP GRADE.—

(*Con.*)

Asphaltum .....	2.0
Whiting .....	35.0

##### BOOT SOLING, HIGH GRADE.

Coarse Para .....	30.0
Sulphur .....	1.0
Litharge .....	15.0
Lampblack .....	1.0
Asphaltum .....	5.0
Whiting .....	48.0

##### BOOT HEELS, HIGH GRADE.

Fine Para .....	5.0
Coarse Para .....	15.0
African grades .....	5.0
Reclaim .....	20.0
Sulphur .....	1.0
Litharge .....	12.0
Asphaltum .....	6.0
Whiting .....	36.0

##### BOOT HEELS, MEDIUM GRADE.

African grade .....	10.0
Reclaim .....	50.0
Sulphur .....	1.0
Litharge .....	8.0
Asphaltum .....	6.0
Whiting .....	25.0

##### BLACK TENNIS SOLING.

Fine Para .....	17.0
Coarse Para .....	17.0
Whiting .....	42.0
Litharge .....	16.0
Lampblack .....	2.0
Sulphur .....	2.0
Plaster of Paris .....	4.0

##### BOOT AND SHOE FRICTION.

Fine Para .....	15.0
African grades .....	25.0
Sulphur .....	1.0
Litharge .....	15.0
Whiting .....	44.0

##### BOOT AND SHOE CEMENT.

Fine Para .....	60.0
Sulphur .....	2.0
Litharge .....	38.0

Dissolve in naphtha to consistency suitable for brush work.



## RUBBER-SHOE VARNISH.

Calcutta linseed oil is placed in an iron kettle over an anthracite fire in a deep fireplace, to carry away the fumes. To the oil are added small proportions of litharge, sulphur and japan drier. The contents of the kettle are slowly boiled for some hours until well thickened. The liquid requires constant attention and frequent stirring to prevent ignition or raising over the top of the kettle. When judged sufficiently boiled, the kettle is removed out of doors and when well cooled the contents are thinned for use to about 50 degrees Baumé with turpentine and naphtha. Care must be exercised that the addition of these volatile liquids be not made under conditions permitting their vapors to find their way to the fire in the varnish house, or disastrous consequences will result. A simple method of preventing this is to place sand bags at the bottoms of the doors of the varnish boiling room.

## DRUGGISTS', STATIONERS' AND SURGICAL SUNDRIES.

THIS part of the rubber business entails more skillful manipulation and more finesse in manufacture than almost any other line. An atomizer bulb, for example, must be graceful in shape, with delicately smooth surface, of good color, and either of the non-blooming variety or so near it that the sulphurous efflorescence will be so slight as to pass unnoticed, while in mechanical goods a length of garden hose may be of any color, may bloom until crusted with sulphur crystals, but if it "stands up to work," it is the best, and is beautiful in the eyes of the trade.

The question of colored rubber is one that has interested this branch of the business from its inception. In none other is so much white rubber made and, incidentally, none others get such good effects. This insistence by customers on white goods and by physicians on black, containing no trace of lead, has entailed a deal of trouble upon this trade, for the manufacturers until recently could not go into the open market and buy a high grade of white recovered rubber, while of black there is ever an ample supply, and for black goods to suit the physician the manufacturer is forced to substitute a dry, bulky

vegetable black for oxide of lead or white lead, and then not get as good a result.

The machinery used is very similar to the equipment of a mechanical goods factory, but the scale is smaller. Washers, grinders, calenders, tubing machines, steam vulcanizers, and small steam presses are the machines used. Special machines are employed in certain parts of the work, but their use is limited to a few factories.

The feature in this trade which stands out most distinctly from other rubber lines is, perhaps, the manufacture of hollow work, as atomizers, syringes, breast-pumps, and a host of other balls and bulbs. The parts for these are cut from sheets of compounded rubber, cemented together at the edges, inflated to the general shape of the mold and cured in open steam heat. In order that the ball may fill the mold perfectly during the cure, a few drops of water or a little ammonia are put inside of it which, vaporizing under the heat, develops pressure enough to perfectly shape it and add to its outer surface the finish found on the inner surface of the mold.

The difficulties that manufacturers in this line experience in making perfect goods are legion, as they are in other lines. They are added to by the fact that the trade, as already indicated, demands articles of beauty from a gum that was designed for utility solely. A trace of black in a white compound may spoil hundreds of dollars' worth of goods, nor can such trace be rubbed off, scoured out, or eradicated, after vulcanization. Hence, white, black, red and other colors must be mixed on separate mills, and the trimmings and scraps kept sedulously apart.

Pure gum—that is, rubber compounded only with sulphur or some other vulcanizing agent—is also largely produced in this line. For example, it makes what is known as dental dam, the pure sheet used by dentists. This is generally a sulphur compound, cured in open steam. Certain manufacturers, however, practice the vapor cure with good success in making these goods. This cure gives a beautiful finish, but if not done with great skill it may be disastrous to both the workman and the goods.

Dental dam, surgical bandages, and stationers' bands represent the highest priced and least compounded goods, while stopples, erasive rubber, and common tubing represent the other extreme. Between the two is a latitude that allows a variety of combinations that no man can number.

COMPOUNDS FOR DRUGGISTS', STATIONERS' AND SURGICAL SUNDRIES.

WHITE BULBS.		TAN WATER BOTTLE.	
Fine Para .....	36.0	Fine Para .....	31.0
Zinc oxide .....	36.0	Whiting .....	48.0
Whiting .....	11.0	White substitute .....	10.0
Ground white scrap .....	11.0	Infusorial earth .....	2.0
Sulphur .....	6.0	Lime .....	0.5
BLACK BULBS.		Golden antimony .....	8.5
Fine Para .....	43.0	WHITE WATER BOTTLE.	
Zinc oxide .....	22.0	Lagos .....	20.00
Whiting .....	10.0	Cameta .....	5.00
Sublimed lead .....	13.0	Zinc oxide .....	42.50
Lampblack .....	4.0	Asbestine .....	8.50
Sulphur .....	8.0	Sulphur .....	2.00
WHITE STOPPERS.		Substitute .....	5.00
Coarse Para .....	10.5	Whiting .....	16.75
Zinc oxide .....	42.5	Lime .....	0.25
Sulphur .....	4.0	MAROON WATER BOTTLE.	
White substitute .....	6.5	Lagos .....	20.00
Asbestine .....	5.5	Cameta .....	5.00
Cotton seed oil .....	3.0	Zinc oxide .....	42.50
Wringer roll dust .....	25.0	Asbestine .....	8.50
Lime .....	3.0	Maroon lake .....	2.00
BLACK STOPPERS.		Sulphur .....	2.00
Pernambuco .....	30.0	Substitute .....	5.00
Sublimed lead .....	5.0	Whiting .....	14.75
Litharge .....	5.0	Lime .....	0.25
Sulphur .....	4.0	PENCIL ERASER.	
Lime .....	10.0	Fine Para .....	17.5
Lampblack .....	4.0	Madagascar .....	17.5
Ground waste rubber .....	42.0	Zinc oxide .....	35.0
AIR CUSHIONS.		Whiting .....	17.5
Fine Para .....	50.0	Pumice .....	10.0
Zinc oxide .....	36.0	Sulphur .....	2.5
Whiting .....	12.5	INK ERASER.	
Sulphur .....	1.5	Fine Para .....	18.5
ELASTIC BANDS (GRAY)		Madagascar .....	18.5
Fine Para .....	94.0	Zinc oxide .....	37.0
Sulphur .....	6.0	Pumice .....	14.5
CATHETERS.		Ground glass .....	8.0
Fine Para .....	43.0	Sulphur .....	3.5
Paris white .....	30.0	SPONGE RUBBER, NO. I.	
Golden antimony .....	12.5	Coarse Para .....	40.0
Substitute .....	3.5	White substitute .....	30.0
Whiting .....	10.0	Sulphur .....	5.0
Vermilion .....	1.0	Whiting .....	10.0
		Alum .....	15.0

COMPOUNDS FOR DRUGGISTS', STATIONERS' AND SURGICAL  
SUNDRIES.—(*Continued*)

SPONGE RUBBER, NO. II.		NON-BLOOMING BLACK.	
Coarse Para .....	25.0	Fine Para .....	35.0
White substitute .....	10.0	Litharge .....	18.0
Whiting .....	50.0	Whiting .....	36.0
Sulphur .....	2.0	Lampblack .....	2.0
Ceresin .....	3.0	Lead hyposulphite .....	9.0
Pine oil .....	2.0		
Ammonium carbonate .....	8.0		

## MACKINTOSHES, PROOFING AND CARRIAGE CLOTH.

THIS business may be handled, in a measure, as the mechanical goods business is; that is, the gums may be mixed by heat on ordinary mixers, and then spread by calenders on the fabrics which give the articles their strength. This is the manner in which rubber surface clothing is run. The machinery is simple, since, in clothing, the parts are cemented together and cured in dry heat. In carriage cloths, after calendering, the goods are grained on embossing rolls, varnished, and run into a dry heat.

The mackintosh and proofing business, however, is somewhat a departure from this. Here the gum, after mixing dry, is usually put in churns with a cheap solvent and reduced to a solution. It is then applied to the cloth with a knife spreader.

For double-texture work, a simple doubling machine brings two surfaces together. A portion of the business that has divided itself from the rest is what is known as proofing for the trade. Here manufacturers simply coat the cloth and sell it to others, who make it up into garments, or anything in fabric or rubber for which there may be a call. The mackintosh manufacturer today is not only familiar with a great variety of rubber gums and ingredients used in compounding, but is also an expert in fabrics, as his business is really closely akin to the tailoring business.

## CLOTHING AND CARRIAGE CLOTH COMPOUNDS.

DULL FINISH CLOTHING.		DULL FINISH HEAVY COATS.	
Fine Para .....	47.00	Fine Para .....	10.0
Reclaim .....	16.00	Reclaim .....	68.0
Whiting .....	16.00	Paris white .....	10.0
Litharge .....	10.50	Lampblack .....	3.0
Coal tar .....	5.50	Litharge .....	5.0
Sulphur .....	2.50	Sulphur .....	0.5
Palm oil .....	1.25	Black substitute .....	2.0
Rosin .....	1.25	Coal tar .....	1.5

## CLOTHING AND CARRIAGE CLOTH COMPOUNDS.—(Continued)

## WHITE SURFACE CLOTHING.

Fine Para .....	24.0
White reclaimed .....	30.0
Whiting .....	20.0
Zinc oxide .....	20.0
Calcined magnesia .....	5.0
Sulphur .....	1.0

## DOUBLE TEXTURE.

Fine Para .....	80.0
Paris white .....	8.0
Litharge .....	9.0
Zinc oxide .....	1.0
Sulphur .....	2.0

## CHEAP DOUBLE TEXTURE.

Lump African flake .....	2.00
Accra buttons .....	3.00
Black substitute .....	28.00
Cheap shoe reclaim .....	23.50
Gilders' whiting .....	26.25
Litharge .....	9.25
Coal tar .....	1.00
Sulphur .....	1.00
Pontianak .....	3.75
Calcined magnesia .....	2.00
Rosin .....	0.25

## GOSSAMER FINISH.

Fine Para .....	53.0
Paris white .....	25.0
Lampblack .....	7.0
Shellac .....	14.0
Sulphur .....	1.0

## TRANSPARENT GOSSAMER.

Fine Para .....	37.0
Central American .....	37.0
Shellac .....	12.5
Substitute .....	12.0
Sulphur .....	1.5

## SINGLE TEXTURE CLOTHING.

Fine Para .....	57.50
Zinc oxide .....	30.00
Litharge .....	8.50
Lampblack .....	3.00
Sulphur .....	0.75
Palm oil .....	0.25

## CEMENT FOR HEAVY COATS.

Fine Para .....	46.0
Whiting .....	31.0
Litharge .....	12.0
Lampblack .....	8.0
Sulphur .....	1.0
Rosin .....	1.0
Coal tar .....	1.0

## CEMENT FOR COATS.

Central American .....	16.0
African flake .....	16.0

## CEMENT FOR COATS.—(Con.)

Whiting .....	30.0
Litharge .....	3.5
Reclaim .....	33.0
Sulphur .....	1.5

## VULCANIZED GOSSAMER.

Fine Para .....	20.0
Whiting .....	62.0
Lampblack .....	8.0
Litharge .....	8.0
Coal tar .....	1.5
Sulphur .....	0.5

## CHEAP GOSSAMER.

Rubber .....	5.00
Reclaim .....	62.00
Whiting .....	17.00
Coal tar .....	3.50
Lampblack .....	1.75
Litharge .....	10.00
Sulphur .....	0.75

## PROOFING.

African flake .....	2.0
Accra buttons .....	10.0
Shoe reclaim .....	40.0
White substitute .....	6.0
Litharge .....	5.0
Calcined magnesia .....	5.0
Paris white .....	26.0
Sulphur .....	1.0
Zinc oxide .....	3.0
Palm oil .....	2.0

## CHEAP PROOFING.

Reclaim .....	33.0
Pontianak .....	16.0
Whiting .....	28.0
Black substitute .....	10.0
Litharge .....	10.0
Sulphur .....	1.5
Coal tar .....	1.5

## CARRIAGE CLOTH, NO. I.

Coarse Para .....	7.00
Reclaim .....	71.50
Whiting .....	14.00
Litharge .....	4.00
Lampblack .....	2.50
Sulphur .....	0.25
Coal tar .....	0.75

## CARRIAGE CLOTH, NO. II.

Coarse Para .....	7.00
Substitute .....	3.50
Reclaim .....	62.50
Paris white .....	10.50
Litharge .....	7.00
Lampblack .....	4.25
Tar .....	2.25
Mineral rubben .....	2.25
Sulphur .....	0.75



## TIRES.

ALTHOUGH the tire business seemed at first to be a natural part of the mechanical rubber goods business, it really proved itself, later, to be a business wholly distinct from it. Even the large manufacturers of mechanical goods who began tire making on a considerable scale, keep this part of their business distinct from other branches as a rule, running it as an entirely separate department. A large business is done in pneumatic tires for bicycles and motor-cycles, but it is much surpassed by the production of pneumatic automobile tires. The knowledge gained through the manufacture of pneumatic bicycle tires (which, by the way, was one of the hardest problems that the rubber trade ever solved) has proved wonderfully effective in developing the skill necessary to make this heavier and more important article. This tire, like the bicycle tire, is built up of frictioned duck, with an outer coating of high-grade rubber carefully vulcanized. While a variety of compounds is used in its make-up, it is true that no manufacturer is able to sell a very low grade of goods, even of unguaranteed quality, because the life of the tire is so important, and the purchaser so desirous for a good article. Cheapening to any great extent is not feasible, particularly in tires sold under mileage guarantee. An adjunct of this business is the manufacture of inner tubes, which has assumed very large proportions.

The general machinery used in making tires is the same that is used in the work of preparing rubber in other lines. There are two general classes of tires manufactured, however: Those that are molded, and those that are made in such a way that they can be wrapped for the process of vulcanization. Wrapped goods, of course, are cured in an open heat. In the one case the tires are cured in presses, sometimes in nests of molds, and sometimes in vulcanizers. Various ingenious and valuable processes and special machines have been invented, and are now in use in this line. An industry that has grown up in connection with the tire business, and has increased the practical knowledge of the uses of rubber wonderfully, is that of tire repairing, which is carried on in many places and to an important extent outside of the rubber factories proper.

A part of the tire business that is of great interest is the making of the solid or cushion molded tire used on light vehicles. Formerly a very large business was done in this, the work being a simple process of mixing the prepared compound, forcing it into shape through a tubing machine, and molding. Of increasing importance is the business of producing heavy solid tires for motor trucks, omnibuses, fire engines, and freight wagons. These are made either by the tubing machine or by building up at the calender from sheeted stock. Many rubber manufacturers have specialized in this line and their yearly product is very great.

## TIRE COMPOUNDS.

## AUTO TIRE TREAD—BLACK.

Fine Para .....	45.0
Zinc oxide .....	25.0
Carbon black .....	10.0
Mineral rubber .....	6.0
Aluminum flake .....	11.0
Sulphur .....	3.0

## AUTO TIRE TREAD—WHITE.

Fine Para .....	44.0
Zinc oxide .....	47.0
Lime .....	1.0
Sulphur .....	3.0
Aluminum flake .....	5.0

## AUTO TIRE FRICTION.

Para .....	30.0
Caucho .....	20.0
Upper Congo .....	20.0
Uncured friction reclaim .....	10.0
Zinc oxide .....	12.5
Lime .....	0.5
Sulphur .....	7.0

## RED AUTO INNER TUBE.

Fine Para .....	75.0
Golden antimony .....	20.0
Zinc oxide .....	4.0
Calcined magnesia .....	1.0

## GRAY AUTO INNER TUBE.

Fine Para .....	92.5
Sulphur .....	7.5

## AUTOMOBILE TIRE-REPAIR

## COMPOUND.

Fine Para .....	28.0
Reclaim .....	26.0
Calcined magnesia .....	8.0
Sulphur .....	12.0
Mineral rubber .....	3.0
Litharge .....	14.0
Infusorial earth .....	6.0
Lime .....	3.0

## INNER TUBE REPAIR

## COMPOUND.

Fine Para .....	34.0
Upper Congo .....	34.0
Sulphur .....	6.5
Black substitute .....	13.5
Infusorial earth .....	10.0
Calcined magnesia .....	1.0
Mineral rubber .....	1.0

## INNER TUBE SPLICING CEMENT.

Fine Para .....	55.0
Sulphur .....	14.0
Litharge .....	14.0
Zinc oxide .....	14.0
Lime .....	3.0

## BEAD CEMENT.

African ball .....	26.0
White substitute .....	4.0
Litharge .....	40.0
Sublimed lead .....	3.0
Asbestos .....	9.0
Whiting .....	8.0
Lime .....	2.0
Sulphur .....	8.0

## BICYCLE TIRE-RIM CEMENT.

Gutta-percha .....	5 pounds
Asphalt .....	10 pounds
Melt together and apply hot.	

## BICYCLE TIRE COVER.

Fine Para .....	64.0
Infusorial earth .....	12.0
Blue lead .....	8.0
Whiting .....	5.5
White substitute .....	5.0
Sulphur .....	5.5

TIRE COMPOUNDS.—(*Continued*)

BICYCLE TIRE—INNER TUBE.		SOLID CARRIAGE TIRE.	
Fine Para .....	80.0	Coarse Para .....	5.0
Zinc oxide .....	9.5	Upper Congo .....	12.0
Blue lead .....	1.5	Zinc oxide .....	24.0
Litharge .....	1.5	Sublimed lead .....	10.0
Paris white .....	3.0	Litharge .....	10.0
Sulphur .....	4.0	Ground solid tire .....	17.0
Lime .....	0.5	Best reclaim .....	19.5
		Sulphur .....	2.5
BICYCLE TIRE FRICTION.		CAB TIRE.	
Fine Para .....	32.0	Para .....	43.75
Accra .....	25.0	Zinc oxide .....	27.50
Cameroons .....	7.0	Infusorial earth .....	23.00
Litharge .....	8.0	Sulphur .....	4.50
Lime .....	2.5	Litharge .....	1.25
Whiting .....	18.0		
Sulphur .....	7.5		
BABY CARRIAGE TIRE.		SOLID TRUCK TIRE.	
Congo .....	10.5	Fine Para .....	40.0
Pontianak .....	8.5	Auto tire reclaim .....	8.0
Floating reclaim .....	10.5	Zinc oxide .....	20.0
Cheap reclaim .....	10.5	Litharge .....	5.0
Substitute .....	8.5	Sulphur .....	4.0
Whiting .....	26.0	Calcined magnesia .....	5.0
Barytes .....	21.0	Mineral rubber .....	3.0
Sulphur .....	4.5	Asbestine .....	15.0

## INSULATED WIRE.

THE manufacture of insulated wire, either with india rubber compound or gutta-percha insulation, is a line that is more distinctly apart from other portions of the rubber business than almost any other. For gutta-percha, the general machinery used is described in the chapter on that gum. Where india rubber is used, the crude gum is treated in the same way as in mechanical goods. It may be forced over the wires by tubing machines, or welded together in strips that are run between grooved rolls.

Braiding machines are also a part of the outfit for weaving the protective covering, and the wire is usually wound on huge drums and vulcanized in open steam heat or in pans under water in open steam. Polishing machines, testing machines, and various mechanical contrivances are, also, a part of this equipment. The line of compounds used is one adapted almost wholly to this industry, and embraces a great variety of ingredients and gums that are treated specifically, under their special heads, elsewhere in this book.

## INSULATION COMPOUNDS.

## WHITE CORE.

Fine Para .....	40.0
Magnesia .....	26.0
Litharge .....	20.0
Whiting .....	14.0

## BLACK CORE.

Fine Para .....	26.0
Magnesia .....	25.0
Lampblack .....	4.0
Litharge .....	20.0
Whiting .....	25.0

## RED ANTIMONY CORE.

Coarse Para .....	36.0
Soapstone .....	50.0
Golden antimony .....	10.0
White substitute .....	4.0

## RED CORE.

Coarse Para .....	20.0
Zinc oxide .....	15.0
Iron oxide .....	5.0
White substitute .....	10.0
Whiting .....	50.0

## UNVULCANIZING INSULATION.

Coarse Para .....	33.3
Balata .....	33.3
Reclaim (not devulcanized) .....	33.4

## GRAPHITE INSULATION.

Coarse Para .....	45.5
Graphite .....	45.5
Sulphur .....	9.0

## HARD WIRE COVERING.

Madagascar .....	14.5
Balata .....	57.0
Sulphur .....	28.5

## SOFT COVERING, NO. I.

Madagascar .....	57.0
Balata .....	28.5
Sulphur .....	14.5

## SOFT COVERING, NO. II.

Central American .....	5.5
Reclaim .....	64.5
Litharge .....	4.0
Silica .....	25.0
Sulphur .....	1.0

## WHITE ELECTRIC TAPE.

African soft ball .....	15.0
Cameroons .....	20.0
African flake .....	10.0
Whiting .....	15.0
Zinc oxide .....	30.0
Sulphur .....	5.0
Rosin .....	5.0

## WHITE ELECTRIC TAPE.

Borneo .....	9.0
African flake .....	22.0
Balsam fir .....	2.0
Whiting .....	55.0
Zinc oxide .....	12.0

## BLACK ELECTRIC TAPE.

Assam .....	12.0
African flake .....	12.0
Pontianak .....	14.0
Barytes .....	32.0
Zinc oxide .....	25.0
Lampblack .....	4.0
Turpentine, crude .....	1.0

## FRICTION TAPE, NO. I.

Fine Para .....	13.0
African small ball .....	13.0
African flake .....	3.0
Best shoe reclaim .....	16.0
Zinc oxide .....	8.0
Barytes .....	13.0
Litharge .....	13.0
Whiting .....	13.0
Sublimed lead .....	5.0
Sulphur .....	3.0

## FRICTION TAPE, NO. II.

Coarse Para .....	15.0
African small ball .....	15.0
African flake .....	1.5
Zinc oxide .....	33.0
Whiting .....	30.0
Sulphur .....	2.5
Cotton seed oil .....	3.0

## MOLDED GOODS MANUFACTURE.

A PART of the rubber business that belongs either to the mechanical or to the druggists' sundries line has, during the past few years, detached itself from the rest, so that today many large factories are run simply in producing small mold

work. They have the usual equipment of rubber machinery, special appliances for filling and emptying molds, and the usual aggregation of hard and soft metal molds that run into thousands of dollars in a short time. The extent to which this business is carried may be imagined when it is known that one company runs 300 presses on this work, and many have from 20 to 50 in constant service. When it is remembered that very rarely are two compounds exactly alike, it will be seen that, in this line also, the expert compounder has a wide field for thought and experiment.

## COMPOUNDS FOR MOLDED GOODS.

## TOUGH MEDIUM HARD VALVE.

Fine Para .....	32.50
Barytes .....	19.25
Litharge .....	9.75
Plumbago .....	8.00
Whiting .....	16.00
Blue lead .....	6.50
Sulphur .....	8.00

## SOFT PUMP VALVE.

Fine Para .....	17.0
Coarse Para .....	26.0
Barytes .....	14.0
Litharge .....	13.0
Whiting .....	13.0
Blue lead .....	13.0
Lampblack .....	0.5
Sulphur .....	3.5

## SMALL ARTICLES, NO. I.

Coarse Para .....	22.00
Blue lead .....	13.00
Whiting .....	32.50
Infusorial earth .....	22.00
Litharge .....	4.25
Sulphur .....	4.25
Lime .....	2.00

## SMALL ARTICLES, NO. II.

Penang .....	34.0
Black substitute .....	7.0
Zinc oxide .....	30.0
Sublimed lead .....	13.0
Litharge .....	13.0
Sulphur .....	3.0

## SMALL ARTICLES, NO. III.

Coarse Para .....	9.0
Reclaim .....	55.0
Barytes .....	22.0
Litharge .....	4.5
Blue lead .....	2.0

## SMALL ARTICLES, NO. III.—

(Con.)

Lime .....	3.0
Sulphur .....	3.0
Cotton seed oil .....	1.5

## SPRINGS.

Coarse Para .....	12.0
African .....	16.0
Ground rubber waste .....	27.0
Litharge .....	13.5
Whiting .....	27.0
Lime .....	0.5
Sulphur .....	4.0

## RED SOFT PUMP VALVE.

Fine Para .....	39.5
Coarse Para .....	39.5
Antimony golden sulphide..	19.0
Sulphur .....	2.0

## MEDIUM PUMP VALVE.

Fine Para .....	8.0
Coarse Para .....	8.0
African thimbles .....	10.5
Barytes .....	16.0
Litharge .....	10.5
Whiting .....	13.0
Soapstone .....	13.0
Blue lead .....	18.5
Sulphur .....	2.5

## LARGE ARTICLES.

Lopori .....	10.00
Black substitute .....	4.00
Ground solid tires .....	65.00
Barytes .....	12.00
Litharge .....	4.00
Lime .....	1.75
Sulphur .....	2.00
Palm oil .....	1.25



COMPOUNDS FOR MOLDED GOODS.—(*Continued*)

BUMPERS.		HOOF PADS.	
Lopori .....	9.0	Guayule .....	10.5
Black substitute .....	4.0	Reclaim .....	10.5
White substitute .....	5.0	Ground cured waste .....	42.0
Ground solid tires .....	16.0	Zinc oxide .....	16.0
Shoe reclaim .....	56.0	Whiting .....	16.0
Infusorial earth .....	2.0	Lime .....	1.0
Litharge .....	4.0	Sulphur .....	4.0
Lime .....	0.5		
Sulphur .....	3.0		
Petrolatum .....	0.5		

## HARD RUBBER.

IN spite of the hundreds of substitutes for vulcanite, or hard rubber, that have been produced, the demand has in no way fallen off, and mills are running full today on the production of this semi-metal. The old-fashioned compound, consisting of 2 pounds of india rubber to 1 pound of sulphur, is still in use in certain goods. Modern progress and chemical knowledge have, however, added a great many compounds for specific uses, so that almost any degree of quality, or hardness, or price, is now furnished on call.

The business, primarily, is a simple one, the hard rubber machinery being like that used in other lines. In the manipulation of the gum for vulcanization, and in its finish, however, special machines are necessary. The finishing machines are lathes, saws, buffers, etc., somewhat similar to what might be used for turning hard wood. The mechanical factories often do a little in hard rubber in the line of valves, and the druggists' sundries mills often make their own syringe fittings, but the bulk of the business in America is done by mills that make only vulcanite the year around.

## HARD RUBBER COMPOUNDS.

SMALL MOLD WORK.		BATTERY BOX.	
Coarse Para .....	38.0	Coarse Para .....	28.0
Madagascar .....	16.0	Balata .....	14.0
Hard rubber dust .....	32.5	Black substitute .....	14.0
Blue lead .....	11.0	Asbestine .....	14.0
Palm oil .....	2.5	Sulphur .....	14.0
		Hard rubber dust .....	14.0
		Cotton seed oil .....	2.0
FINE TUBING.		SHEETS.	
Fine Para .....	25.00	Fine Para .....	27.50
Substitute .....	8.00	Pinky Madagascar .....	27.50
Zinc oxide .....	60.00	Sulphur .....	41.00
Sulphur .....	4.25	Lime .....	2.75
Palm oil .....	2.75	Beeswax .....	1.25

HARD RUBBER COMPOUNDS.—(*Continued*)

RODS.		RED MOLDED.—( <i>Con.</i> )	
Pinky Madagascar .....	13.00	Vermilion .....	14.0
Congo ball .....	8.00	China clay .....	7.0
Borneo .....	5.25	Sulphur .....	18.0
Hard rubber dust .....	44.00	Palm oil .....	1.0
Sulphur .....	23.50	SEMI-HARD.	
Cotton seed oil .....	4.00	Fine Para .....	34.0
Beeswax .....	0.75	Sublimed lead .....	17.0
Lime .....	1.50	Zinc oxide .....	17.0
SYRINGE PIPES.		Litharge .....	17.0
Fine Para .....	53.5	Lampblack .....	11.5
Sulphur .....	28.5	Sulphur .....	3.5
Hard rubber dust .....	18.0	COMBS.	
RED MOLDED.		Fine Para .....	53.0
Fine Para .....	53.0	Sulphur .....	47.0
Red oxide .....	7.0		

## CEMENTS.

MANY rubber factories are run wholly on this line of work, the gums being mixed as in a general rubber business, put into solution in churns, and sold by the barrel for an infinite variety of purposes. Hundreds of different formulas are in use for cements intended for general and specific purposes. The leather shoe business, for instance, calls for a dozen or more special cements. The bicycle business has need for a great many grades of what are known as tire cements. Stickiness, waterproof qualities, durability, and cheapness in their goods are sought by all cement manufacturers, and, in order to secure these qualities, they demand skill in compounding in no way inferior to that shown in other lines of rubber work.

## CEMENT COMPOUNDS.

PURE-GUM CEMENT.		LEATHER SOLE CHANNEL, NO. I.	
Fine Para dissolved in benzol or naphtha.		Fine Para (washed) ..	30 pounds
WHITE (CURING).		Rosin .....	5 pounds
Fine Para .....	20 pounds	Naphtha .....	40 gallons
Zinc oxide .....	12 pounds	LEATHER SOLE CHANNEL, NO. II.	
Sulphur .....	2 pounds	Fine Para (washed) ..	10 pounds
Naphtha .....	25 gallons	Rosin .....	5 pounds
YELLOW (CURING).		Naphtha .....	40 gallons
Fine Para .....	20 pounds	HARD-RUBBER CEMENT.	
Litharge .....	8 pounds	Fine Para .....	30 pounds
Zinc oxide .....	8 pounds	Sulphur .....	10 pounds
Sulphur .....	2 pounds	Naphtha .....	12 gallons
Naphtha .....	25 gallons		

CEMENT COMPOUNDS.—(*Continued*)

## LEATHER WELTING.

Fine Para .....	10 pounds
Sulphur .....	5 ounces
Naphtha .....	10 gallons

## LEATHER SOLE-LAYING.

Lagos buttons or strips	10 pounds
Pontianak .....	5 pounds
Naphtha .....	20 gallons

## LEATHER BELTING, NO. I.

Carbon bisulphide ....	20 pounds
Oil of turpentine .....	2 pounds
Gutta-percha sufficient to form a paste.	

## LEATHER BELTING, NO. II.

Caoutchouc .....	6 pounds
Shellac .....	4 pounds
Carbon bisulphide ....	40 pounds
Turpentine .....	4 pounds

## DAVY'S UNIVERSAL.

Gutta-percha.	
Common pitch.	
Equal parts of each melted together.	

## FINE "DIPPED" WORK.

Fine Para .....	2 pounds
Carbon bisulphide ....	60 pounds
Absolute alcohol .....	4 pounds

## MARINE GLUE, FRENCH.

Dissolve 10 pounds caoutchouc in naphtha and add 20 pounds shellac. Melt until mixed and pour while hot on metal plates to cool.

## DENTAL AND STAMP GUM.

THE manufacture of unvulcanized gums for the use of dentists and rubber-stamp manufacturers is an industry apart from other lines, and one that has assumed large proportions. The rubber is compounded and sold by the manufacturer, and cured and finished by the dentist or rubber-stamp manufacturer. In stamp work the rubber is compounded for soft rubber and many hundreds of tons are sold during the year, while, of course, the dental rubber is so mixed that under the cure it becomes vulcanite of the color desired. The machinery for this work consists chiefly of washers, mixers, and calenders.

## DENTAL AND STAMP GUM COMPOUNDS.

## DENTAL—LIGHT PINK.

Fine Para .....	16.0
Lithopone (green seal)....	56.0
Lac sulphur .....	6.0
Lime .....	2.0
Pale vermilion .....	20.0
Ultramarine blue .....	Trace

## DENTAL—BLACK PALATE.

Fine Para .....	77.0
Lac sulphur .....	15.0
Lampblack .....	4.0
Lime .....	4.0

## DENTAL—RED PALATE.

Fine Para .....	62.5
Lac sulphur .....	12.5
Dark vermilion .....	22.0
Lime .....	3.0

## DENTAL—BLACK WEIGHTED.

Fine Para .....	20.5
Lac sulphur .....	15.5
Lime .....	1.0
Pure tin foil .....	61.5
Raw linseed oil .....	1.5

## STAMP GUM, NO. I.

Fine Para .....	44.0
Whiting .....	9.0
Zinc oxide .....	11.0
Talc .....	9.0
Litharge .....	18.0
Lime .....	1.0
Mineral rubber .....	2.0
Sulphur .....	6.0

DENTAL AND STAMP GUM COMPOUNDS.—(*Continued*)

STAMP GUM, NO. II.		STAMP GUM, NO. III.	
Fine Para .....	20.0	Fine Para .....	17.0
Coarse Para .....	20.0	Borneo .....	34.0
Whiting .....	20.0	Litharge .....	8.5
Zinc oxide .....	27.0	White Lead .....	8.5
Litharge .....	10.0	Whiting .....	8.5
Sulphur .....	3.0	Lime .....	6.5
		Barytes .....	8.5
		Sulphur .....	8.5

## NOTIONS.

THIS department of the rubber business, the importance of which is not generally appreciated, is that which takes in such work as waterproof dress bindings, dress shields, children's aprons, diapers, etc. Several large factories manufacture these goods, mixing their rubber by the usual processes, coating it on calenders, and having special machines for forming and curing the goods in their special shapes. In the manufacture of dress shields the vapor cure is often practiced very successfully. The rubber manufacturers of this class are not by any means inexpert compounders. They have also, perhaps, gone as far as any in deodorizing rubber goods so that the smell of the gum or any compounding ingredients is wholly done away with.

## NOTION-TRADE COMPOUNDS.

DRESS SHIELDS.		WHITE BATHING CAP.	
Fine Para .....	45.0	Fine Para .....	75.0
Zinc oxide .....	25.0	Zinc oxide .....	20.0
White substitute .....	14.5	Sulphur .....	5.0
Litharge .....	12.5	Calcined magnesia .....	3.0
Sulphur .....	3.0		
BLUE SHEETING—VAPOR CURE.		CRIMSON BATHING CAP.	
Fine Para .....	56.5	Fine Para .....	87.0
Zinc oxide .....	38.0	Soluble oil red .....	5.0
Ultramarine blue .....	5.5	Sulphur .....	5.0
WHITE SHEETING—VAPOR CURE.		Calcined magnesia .....	3.0
Fine Para .....	60.0		
Zinc oxide .....	40.0		
NURSERY SHEETING.		BLUE BATHING CAP.	
Fine Para .....	39.0	Fine Para .....	87.0
Zinc oxide .....	29.0	Soluble oil blue .....	5.0
Whiting .....	29.0	Sulphur .....	5.0
Sulphur .....	2.5	Calcined magnesia .....	3.0
Palm oil .....	0.5		

## PLASTERS.

THERE are few factories that keep wholly to this line of work. It is, perhaps, as simple as any part of the rubber business, a fair grade of rubber being washed, dried, and mixed by the usual methods, and calendered upon the fabric that forms the base of the plaster. These goods are not vulcanized, of course. Though a variety of gums and medicaments are used in this compounding, the range is probably smaller than any other line of rubber manufacture.

## PLASTER COMPOUNDS.

## POROUS PLASTER.

Fine Para .....	50.0
Burgundy pitch .....	25.0
Gum olibanum .....	25.0
Medicated as desired.	

## MUSTARD PLASTER.

Fine Para .....	3.0
Vaseline .....	75.0
Benzine .....	22.0

The plaster surface is dusted over with mustard flour after application to the cloth.

## MENTHOL PLASTER.

Fine Para .....	30.0
Gum olibanum .....	15.0
Burgundy pitch .....	15.0
Rosin .....	15.0
Orris root .....	15.0
Beeswax .....	8.0
Menthol .....	2.0



## CHAPTER XX.

### GUTTA-PERCHA—ITS SOURCES, PROPERTIES, MANIPULATION AND PRINCIPAL USES— TYPICAL COMPOUNDS—BALATA.

GUTTA-PERCHA, which was introduced into Europe from Singapore in 1843, was for a while confounded with india rubber, from which it differs in some very important particulars. It becomes soft and plastic on immersion in hot water, retaining the shape then given it on cooling, whereupon it becomes hard, but not brittle, like other gums. India rubber, on the other hand, does not soften in hot water, and retains its original elasticity and strength unimpaired. The water, as such, exercises no softening action on gutta-percha, the effect being purely one of temperature, which may equally well be produced by hot air, only somewhat more slowly. The degree of heat required depends upon the quality of the material, but even the hardest kinds become plastic above 150 degrees F. Heated in air considerably above the boiling point of water, gutta-percha decomposes and finally ignites, burning with a luminous smoky flame and emitting a pungent odor resembling that from burning rubber. If heated in a vacuum, gaseous and liquid products are obtained similar to those resulting from the distillation of rubber. The liquid which distils over consists chiefly of hydrocarbons of the terpene series, which form an excellent solvent for caoutchouc. The two most important are *isoprene* and *caoutchine*, which are identical with the liquids by the same names obtained from india rubber. Since these products can also be obtained from other sources, Dr. Eugene Obach and others have observed that they may yet form a stepping-stone in the synthetical production of india rubber and gutta-percha from the lower terpenes.

A curious physical characteristic of gutta-percha is that when it has been softened in water, although it is so plastic that it will reproduce the most delicate impressions, it will withstand blows from hammers or may be thrown against

stone without being marred. The reason is that it contains a large amount of air. By subjecting gutta-percha to a vacuum, a large amount of air is withdrawn from the gum, and it loses its property of hardening on cooling, its substance being like a tough, greasy leather.

Nowhere on the globe have genuine gutta-percha trees been found outside of an area embracing portions of the Malay peninsula, Borneo, Sumatra, and adjacent islands. These trees belong to the natural order *Sapotaceæ*; the principal genera and species will be noted further on.

Pure gutta is insoluble in ether and light petroleum spirit at ordinary temperatures, whereas both albane and fluavile dissolve readily in them. Gutta possesses all the valuable qualities of gutta-percha, but in a much enhanced degree; it becomes soft and plastic on heating, and hard and tenacious on cooling, without being in the least brittle. But the resins themselves at ordinary temperatures are either soft or quite friable. It is, therefore, gutta which forms the useful constituent of gutta-percha, and the resins are only accessory components, which, although admissible, and perhaps, even desirable in a comparatively small amount, yet have a decidedly detrimental effect when they preponderate. Hence, in order to determine the technical value of a sample of gutta-percha, it is necessary first to learn the relative proportion or ratio between gutta and resins. There must also be taken into account the *water* enclosed in the mass, and the coarse impurities—wood fibers, bark, sand, etc.—which are described as *dirt*. These components represent the loss or waste to the manufacturer.

While the relative proportion of gutta and resins forms an important criterion for estimating the commercial value of a sample, it is not in itself sufficient. Although the analysis of two different specimens may give the same result, the physical and mechanical properties, and, most important of all, the durability, may differ widely, owing to a difference in their molecular constitution. It will thus be seen that there are guttas and guttas. In addition to the qualitative analysis, it is necessary to scrutinize the gutta itself, which requires much judgment and experience. Analyses have been made of speci-

mens which contained eight times as much gutta as resin; others contained about an equal amount of both, and in still others the amount of resin was three times that of gutta. Samples in which the percentage of resin reaches that of gutta, or surpass it, are of a decidedly inferior description. These differences are due doubtless to the fact that the gutta-percha of commerce is derived from trees of various species, and also in part to the treatment which the gum receives at the hands of the gatherers, who are suspected of mixing the product of different trees, to say nothing of adulterations of a more debasing character.

The commercial classification of gutta-percha is less satisfactory than that of india rubber, since no standards have become fixed in the markets. While Para rubber, for instance, may be bought and sold by means of established designations, "Islands fine," "Upriver fine," and the like, no such practice exists with regard to gutta-percha. Since all transactions in the latter are based upon samples, trade names and brands are little considered. However, "Macassar," and "Bandjermassin," which are the names of districts producing gutta-percha, were formerly used to indicate the highest quality, while "Sumatra" sorts were supposed to be less valuable, and "Borneo" the lowest of all. In a sense these designations have become merely commercial, no longer affording any indication of the origin of the gutta-percha. At the same time, "Macassars" and "Bandjermassins" might vary with every new arrival, so that one was not certain, in buying one of the sorts named, to obtain particularly good gutta-percha; it might have been the very opposite.

Innumerable sorts appear in the Singapore market—which is the center of the gutta-percha trade; but Dr. Obach selected twelve of the principal brands as typical of all the rest, and divided them into four groups, for convenience in comparison, the best being named first. They are as follows, the designations being derived either from the countries of their origin or from the places of export:

- |     |   |   |
|-----|---|---|
| I.  | { | 1. Pahang—from the Malay peninsula.               |
|     | { | 2. Bulongan red—from Macassar, Borneo.            |
|     | { | 3. Bandjer red—from Bandjermassin, South Borneo.  |
| II. | { | 4. Bagan goolie soondie—from Borneo.              |
|     | { | 5. Goolie red soondie—from Serapong, Borneo.      |
|     | { | 6. Serapong goolie soondie—from Serapong, Borneo. |

- |      |   |  |
|------|---|--|
| III. | { | 7. Bulongan white—from Macassar, Borneo.           |
|      | { | 8. Mixed white—from Borneo.                        |
|      | { | 9. Bandjer white—from Bandjermassin, South Borneo. |
| IV.  | { | 10. Sarawak mixed—from Borneo.                     |
|      | { | 11. Padang reboiled—from Sumatra.                  |
|      | { | 12. Banca reboiled—from Banca.                     |

Group I comprises the three best kinds, derived from trees of the genus *Dichopsis* (known in continental Europe, as *Palaquium*). Group II comprises three kinds of the second order, derived probably from the genus *Payena*. Group III embraces the so-called "white gutta," of second and third grade, mostly of uncertain origin, but probably from *Dichopsis polyantha*. Group IV is made up of mixed materials, two of them being what is termed "reboiled," an operation performed by the Chinese traders, who buy up odd lots, soften the materials in hot water, and make them into a more or less homogeneous average mixture. The "Sarawak mixed" lots mostly represent a very useful second-class material; the "reboiled" is decidedly inferior. This classification is based upon the results of 751 analyses of mixed lots, representing over 5,000,000 pounds of raw gutta-percha, made by Dr. Obach, with a view to arriving at the relative proportions of gutta, resin, dirt, and water contained. The cleanest kind is the "Sarapong soondie," which contains only  $3\frac{1}{2}$  per cent. of dirt, but it is rather wet, having more than 25 per cent. of water. One of the least favorable materials is "Bandjer white," which contains 33 1-3 per cent. of water and 15 per cent. of dirt, making in all nearly 50 per cent. of waste. When a raw material is very dirty and wet, it is noticeable on cutting the blocks open, and this is now the rule in the Singapore market. The blocks are then sorted out into several grades (two or three, sometimes more), according to their appearance, and valued accordingly.

A grade of gutta-percha which is nearly white in color and very brittle is apt to contain a large percentage of resin, which, as already explained, renders it of little value. In explanation of some of the terms in the preceding classification, it may be said that gutta-percha is obtained principally by cutting down the trees and ringing the bark at intervals of 12 to 18 inches along the trunk. The milky sap in a little while fills the grooves cut into the bark, and, in the better varieties, soon coagulates, when it is scraped off with a knife. In the case

of inferior sorts, the milk requires more time to curdle, and has to be caught in receptacles placed under the tree. The collected milk is then gently boiled, either by itself or with the addition of water. The material obtained without the use of water is called a *goolie*, the other a *gutta*; but the two kinds are often mixed together. The *goolie* is more compact than the *gutta*, and has a dough-like smell. The word *soondie* is derived from the Malay term "gutta-sundek," which is applied to the product of trees of the *Payena* species already referred to.

The processes employed by manufacturers for cleaning raw gutta-percha are either *mechanical* or *chemical*. Those of the first class will first be considered. Generally speaking, the raw gutta-percha is either first cut up in a slicing machine and then softened in hot water, or the lumps are placed directly in hot water and the soft material transferred to the washing machine. There it is washed with hot water for a longer or shorter time, and then passed through a strainer. Next, as a rule, it is washed once more, then put into a kneading or masticating machine, to consolidate it and remove the mechanically enclosed water, and finally it goes to the rolling mill, to be made into sheets.

The slicing machine or chopper now used is pretty much the same as that proposed by Charles Hancock, of England, in his patent (No. 11,575, O.L.) of 1847, except that it is provided with a greater number of fluted and serrated knives, instead of only three plain ones, fixed in the slots of a heavy iron disc. The blocks of gutta-percha are packed into a trough and then forced against the rotating disc, the knives in which cut the material into thin slices.

The washing machine consists of an iron roller of star-shaped section, enclosed in a cylindrical shell provided with one or two projections, or ribs, against which the gutta-percha is forced in going around. The cylindrical shell is enclosed in a large iron case, filled with water, which is heated by means of direct steam. The dirt, as it is washed off, falls through the lower part of the cylindrical shell into the outer case, whence it is drawn off periodically. This machine is developed from that described in the English patent of R. A. Brooman (No. 10,550, O. L.).



The gutta-percha leaves the washing machine in a plastic state and passes to the straining machine—a strong iron cylinder with a perforated bottom, on which a number of discs of fine wire gauze have been placed. It has a piston which is driven home by hydraulic power, at a pressure of 1,500 to 2,500 pounds per square inch, squeezing the soft gutta through the meshes of the gauze.

The kneading machine or masticator resembles the washer, except that the roller is smaller in diameter, and the flutings are more numerous and not so deep. The gutta-percha is kept hot during mastication and the water escapes in the form of steam through openings at the top.

The mixing machine, introduced by Paul Pfeiderer, is similar to that used in the india rubber, linoleum, and other similar industries. It is provided with peculiarly shaped blades, working against one another. The machine is used for mixing the various sorts of gutta-percha, in order to obtain a material of requisite properties, and also for blending gutta-percha with pigments or other ingredients. The rolls can be heated by steam, but heat is developed by the kneading process itself, and care must be taken not to overheat the material.

The gutta-percha is next rolled into sheets, usually between  $\frac{1}{8}$  and  $\frac{1}{4}$  inch, and cut into lengths of 5 or 6 feet, and stacked away for use. The rolling machine takes the material from the mixer and squeezes it between parallel rollers, running it back and forth until it is cool and hard enough for cutting up.

The average percentages of waste, shown by numerous analyses of the twelve brands of gutta-percha catalogued on a preceding page, are about as follows:

Pahang .....	34	Bulongan white .....	43
Bulongan red .....	35	White mixed .....	35
Bandjer red .....	44	Bandjer white .....	47
Bagan goolie soondie .....	32	Sarawak mixed .....	44
Goolie red soondie .....	27	Padang reboiled .....	44
Serapong soondie .....	36	Banca reboiled .....	29

The difference in the quality of various brands of gutta-percha, measured by the relative proportions of gutta and resin, has already been mentioned. Of the sorts mentioned

above, "Banca reboiled" shows a comparatively small loss in cleaning, but it is the least valuable on the list, being low in gutta, whereas "Pahang," though losing more in the cleaning process, is by far the most valuable sort in the market, because so rich in gutta. Gutta-percha imported in recent years loses more in cleaning than formerly; Dr. Obach, in 1898, estimated the loss as almost twice as great as formerly.

The chemical washing process was suggested by Charles Hancock, in an English patent, in 1846. He steeped raw gutta-percha, cut into small pieces, in a solution of caustic alkali or chloride of lime, to neutralize the acidity and remove any unpleasant odor. His experiments showed that the alkaline treatment not only reduced the percentage of dirt—that is, it was better cleaned than by the mechanical process—but lessened the capacity of the gutta-percha for retaining mechanically enclosed water. But the treatment with chemicals requires great care and judgment, and thorough subsequent washing with water; otherwise the material will be rendered perishable.

Chemicals were also used by Obach for hardening gutta-percha. The really valuable constituent of gutta-percha being the gutta, the more a sample contains of the latter, the better it is, provided the gutta itself is of a good description. For certain purposes it is advantageous to improve the hardness and other mechanical properties of gutta-percha, and this can be done by extracting the resin with a suitable solvent, which leaves the gutta itself intact. The raw gutta-percha is first chopped and thrown on drying platforms gently heated from below by steam pipes. Or the pieces may be thrown into a rotating drum heated by currents of warm air. They then go to a series of tanks in which petroleum spirit is used as a solvent for the resin. The spirit becomes charged with the resinous matters, and the resulting solution is distilled off, after which the material remaining is masticated as in the case of any other gutta-percha. A specimen treated by this process will remain quite hard under a temperature which will render other specimens soft and plastic. Other liquids may also be used, as ether, and a saturated solution of carbon disulphide in alcohol.

Instead of removing impurities from gutta-percha by washing it either with water or an alkali, this can be done by dissolving the material into a suitable liquid, straining or filtering the solution, and then evaporating the solvent. Carbon disulphide has been used as the solvent, but with the effect of rendering the gutta-percha perishable.

Recently an article known as green gutta-percha has been offered to the trade, being extracted from the leaves of the trees. Several systems for extracting gutta-percha from leaves have been described. That of Dieudonne Rigole involves the use of carbon disulphide; that of Eugene Serullas the use of hot toluene as a solvent, after which the gutta-percha is precipitated by means of acetone, instead of distilling off the solvent; and that of Obach the use of light petroleum spirit as a solvent for leaves that have been previously crushed between rollers, the gum being reprecipitated from the solution on cooling below 60 degrees F. The author of each process has devised apparatus for its operation.

Many trees produce gums which have been experimented with in the hope that they would prove good substitutes for gutta-percha, but none have proved of value except the "bullet" tree, which yields balata. The gutta contained in balata is very strong and tough, being of excellent quality; but the percentage of resin is large, and the material can be regarded as a substitute only for second-class; or, perhaps, even third-class, gutta-percha. Balata is somewhat more flexible than gutta-percha, containing an equal amount of resin, which appears to be due to the softness of the resinous constituents. On becoming heated balata behaves much like ordinary gutta-percha. If plunged into boiling water it becomes quite soft and plastic. If next immersed in cold water, it slowly hardens again, but still remains flexible and elastic, showing no signs of brittleness. Analyses of specimens of balata from British Guiana, obtained from the London docks in 1889-94, showed an average loss of 13.8 per cent. of water, and 9.9 per cent. of dirt, or a total of 23.7 per cent. of water. The respective percentages of gutta and resin were 41.4 and 34.8.

The specific gravity of cleaned gutta-percha is practically the same as that of water, though varying with the relative

proportion of gutta and resin, becoming lower as the percentage of resin increases. It may be affected, also, by the constitution of the resin and also of the gutta. The softening temperature of gutta-percha depends entirely upon the ratio of gutta and resin. A specimen of which 60 per cent. was resin was softened at the temperature of 48 degrees C. to the same extent as another specimen, containing only  $2\frac{1}{2}$  per cent. of resin, for which a temperature of 55 degrees C. was required. The time for the material to become hard again, after having previously been softened in hot water, depends in a like degree upon the proportion of gutta and resin. But the principal mechanical property of gutta-percha with which the manufacturer has to deal is the tensile strength. A specimen having 45 per cent. of gutta and 55 per cent. of resin will break under pressure of 770 pounds to the square inch, whereas for another specimen, after most of the resin has been extracted with petroleum spirit, nearly twice that breaking strain will be required. As for the elongation of gutta-percha—*i. e.*, the extent to which it will stretch before breaking—it is also affected by the percentage of resin, being in the last two cases, for instance, 490 and 500 per cent., respectively, but it also depends on the nature of the gutta.

The earliest practical use of gutta-percha was for surgical appliances—for bandages, splints, and receptacles for vaccine virus. It is used for ear trumpets; for the handles of surgical instruments, as it affords a firm grip and is preferable to wood for antiseptic reasons; in medicine, in the form (1) of a very thin tissue, (2) of sticks, and (3) of a 10 per cent. solution in chloroform; for chemical purposes, in the form of tubes, pumps, syringes, bottles, and the like, and for ladles and tubes for handling caustic alkalies and corrosive acids and liquids in chemical works; and for mechanical purposes, as rings and cups for pumps and hydraulic presses and for driving bands (belting). For the latter purpose balata is also used largely, interposed between canvas; such belts can be joined by means of a solution of balata or gutta-percha in carbon disulphide. Another application of gutta-percha is that for taking impressions of medals, and also of the interior of large guns. Gutta-percha is also modeled into ornaments in

the shape of the leaves and petals of flowers, this being done by working the gum by hand in hot water with one or two simple iron tools. Such ornaments are often applied to the decoration of jars made of semi-porous ware, the whole being painted afterward.

But the most important application of gutta-percha is in the insulation of submarine and subterranean cables. Dr. Werner von Siemens first proposed gutta-percha for insulating purposes in 1846, and in the next year he designed a screw press, for the seamless covering of wires with that material, which is still in existence, while the principle of the press is still adhered to. Gutta-percha has been found to be very permeable to the X-rays, and it has been proposed to utilize this property to examine gutta-percha-covered wires for the detection of defects in the copper conductor, particularly in "joints," or for finding air-bubbles. The X-rays may also be used for the detection of large foreign bodies in the raw gutta-percha.

The electric properties of gutta-percha depend chiefly on the nature of the gutta and to a less extent upon the resin; but only very slightly on the relative proportion of these two components. They depend also upon the nature and amount of the impurities and on the water. The insulation and inductive capacity are little affected by the extraction of the resin. The insulation should be as high as possible, and the inductive capacity, for most purposes, as low as possible, but whereas the latter is mostly associated with other good qualities of the material, such is not always the case with a high insulation. A third electric property is called dielectric strength, or resistance to piercing by high voltage. A thickness of a little over  $\frac{1}{8}$  inch of gutta-percha breaks down with 40,000 volts, and one of about 1-10 inch with 28,000 volts.

Gutta-percha hardened by the extraction of its resin is used chiefly in the manufacture of golf balls. Gutta-percha for this purpose should be tough, elastic, and not brittle at low temperatures; it should be specifically lighter than water, in order not to sink if dropped accidentally into a ditch. It is requisite that the proper grade of raw material be chosen and that the resin be extracted as completely as possible. To test



the elasticity of golf balls, a machine is used, consisting of (1) a perpendicular scale, divided into feet and tenths; (2) a clip, at the top, for holding the ball to be tested; and (3) an iron plate at the bottom. The object is to measure the rebound of the ball, when released from the clip and falling upon the plate. A ball made of gutta-percha, of which 25 per cent. was resin, rebounded only to the point on the scale marked 30; a ball containing only 10 per cent. resin rebounded to 45; and still another, having only a small percentage, rebounded to 60—the highest point reached. A ball of balata, having the resin thoroughly removed, rebounded to 59.

Some figures will give an idea how greatly the physical and mechanical properties of gutta-percha are affected by the extraction of the resin. Carefully selected specimens of a medium quality were cut fine and intimately mixed, and then divided into two portions. One portion was next washed in the ordinary way with water; the other treated with petroleum spirit until nearly all the resin had been extracted. The two specimens showed the following analyses:

	Gutta	Resin	Dirt	Water	Total
Cleaned in ordinary way.....	54.7	39.4	2.7	3.2	100
Same material, hardened.....	93.0	2.8	2.5	1.7	100

The different physical and mechanical properties of the two specimens are indicated in the next comparison:

	Ordinary	Hardened
Temperature when commencing to soften..	37.7° C.	57.2° C.
Temperature when commencing to harden.	58.8° C.	91.1° C.
Time of hardening .....	17 min.	45 sec.
Tensile strength—pounds per square inch..	1,592	5,662
Elongation—per cent. ....	360	285

The electrical properties, on the other hand, are but little affected, the insulation being practically the same as before, and the decrease of specific inductive capacity is probably due to the smaller percentage of water in the hardened material.

The principal cause of the destruction of gutta-percha is the absorption of atmospheric oxygen, which alters the gutta and produces a brittle resin of quite a different nature to that originally present in the material. This destructive oxidization is greatly assisted by light, and by other causes—for instance, by any action tending to make the material porous, such as alternate wetness and dryness, the presence of sub-

stances which exercise a solvent action on gutta-percha as a whole or any of its components. Certain alkaline substances and decaying organic matters also appear to act injuriously, but frequently it is impossible to assign a definite cause for decay of gutta-percha. It is, however, not merely manufactured gutta-percha which undergoes these destructive changes, for raw material of the very best kind succumbs in time to the combined action of light and air. On the other hand, specimens of gutta-percha are in existence which, after proper means of protection, have remained in good condition for more than fifty years. Complete immersion in water affords a good protection, for which reason submarine cores of gutta-percha are more safely placed than underground wires. Another way of excluding the air, to some extent, is to varnish the gutta-percha articles. When the gutta-percha is oxidized it becomes porous and full of cracks. If it be used for insulating wires, the insulation fails at such places, since the moisture penetrates the pores and fissures and establishes an electric contact with the conducting wire.

Some compounds containing gutta-percha are very useful for different purposes, and a specially useful one, consisting of a mixture of gutta-percha, colophony, and Stockholm tar, is known as "Chatterton's compound." It is used largely in connection with the manufacture of gutta-percha-covered wires, as a binding material between the copper conductor and the gutta-percha covering, or between the different layers of gutta-percha on the core.

Willoughby Smith patented the following compound for insulating wires: one-fifth by weight of Stockholm tar and about the same weight of resin are put into a vessel with a jacket (or, preferably, a series of pipes) heated by steam; when properly melted the whole is passed through a wire gauze strainer "into another vessel similarly heated"; three-fifths by weight of gutta-percha, having by preference been previously cleansed in the ordinary way and reduced into thin pieces or shreds, is then put into the heated vessel and mixed with the resin and tar. In this second vessel are stirrers, for mixing the whole uniformly.

Leonard Wray's cable compound was made of 1 part

gutta-percha, 4 parts india rubber, 2 parts shellac, 2 parts flour of glass. This was used for underground wires.

Gaullie combined gutta-percha with Roman cement by means of animal gall, forming a plastic material, capable of being stamped and molded.

Cooley mixed gutta-percha with resin oil under heat, then mixed in carbonate of soda with roasted starch. To this compound he added asphalt to make it harder, or hyposulphite of lead, to make it softer. He also made a great many gutta-percha compounds in which salts were present. These he steeped in water after mixing until they became soft and flexible.

Charles Macintosh made a compound for telegraph wire from gutta-percha, naphthalene, and lampblack.

Charles Hancock boiled gutta-percha in muriate of lime, passed it between heated cylinders, sifting the surface with rosin, in the production of a compound for complete insulation. Another of his compounds was made of gutta-percha, shellac and borax. He also made gutta-percha sponge by mixing with it carbonate of ammonia or alum and applying heat. He also made a hard gutta-percha which was similar to vulcanite by mixing it with sulphur, putting it in molds and keeping the compound at a high temperature for several days.

Duncan invented a great many compounds for gutta-percha cement, many of which are now in general use. One suggestion of his was the mixing of gutta-percha with Canada balsam and shellac, the resultant compound being a good cement capable of standing considerable heat and in no danger of becoming greasy on its surface.

Robert Hutchinson claimed that he was able to render gutta-percha less liable to oxidize, to improve its elasticity, increase its tenacity, and diminish its liability to become sticky, or tacky, by compounding it with lanichol or wood cholesterin. (See Lanoline).

Forster deodorized gutta-percha by mixing with it essential oil, orris root, or gum benzoin.

Liquid gutta-percha is gutta-percha dissolved in chloroform, to which a little carbonate of lead is added in the shape of a fine powder. After agitation, the mixture is set aside

until the insoluble matter has settled. The clear liquid is then decanted.

Spill, in order to prevent gutta-percha that had been vulcanized from being attacked by grease, treated it to a solution of melted beeswax, hardening this coating with an infusion of nut-galls.

Godefroy mixed gutta-percha with powdered coconut shell, claiming that it would stand a higher degree of heat, and was considerably more elastic. Day, in America, mixed pipe clay with gutta-percha to prevent its sponging during vulcanization.

The vulcanization of gutta-percha, in spite of a common impression to the contrary, is something that can be easily accomplished, and is analogous to the vulcanization of india rubber. It can be done by mixing with free sulphur or sulphides that contain free sulphur, or by the use of chloride of sulphur. As the Parkes mixture attacks gutta-percha very easily, the dipping for vulcanization must be very quick, the article afterward being allowed to remain in the air for some hours. The second dip can be a little longer, as the surface is less easily attacked than before. The vulcanized product is quite hard and will stand a high degree of heat. Chloride of sulphur mixed with bisulphide of carbon can also be incorporated in a solution of gutta-percha and bisulphide of carbon, with the result that the gutta-percha will be thoroughly vulcanized.

The late Robert Dick, of Glasgow, who was a successful manufacturer of gutta-percha articles in the mechanical line, produced many vulcanizable compounds of gutta-percha of great value, some of which follow. He claimed that his compounded gutta-percha retained the good qualities of the gum; that is, that it was homogeneous and plastic at a moderate heat, but tough and hard at ordinary temperatures, and that it was just as valuable afterward for mixing and molding over again.

Compound No. 1 is described as the hardest and toughest, and may be used, in place of leather and vulcanized india rubber for tires, belts, pulley coverings, horse shoes, etc. No. 2 is softer and more elastic, and suitable for soles and heels of shoes, wringer rolls, springs, playing balls, mats, etc. These

goods are mixed in the usual way, and vulcanized in the masticator, but not enough to take away the plastic qualities of the gutta-percha. For treating this compound, a special masticator was devised by Mr. Dick, the rolling cylinders being hollow, and a Bunsen gas-burner inserted through one end of the hollow axle, while the gases pass off at the other, thus heating both roller and mixture. The outer cylindrical masticator is jacketed and heated with steam:

## COMPOUND NO. I.

Pure cleaned hard gutta-percha.....	28
Pure cleaned tough selected gutta-percha or balata (preferably more rather than less) .....	11
Pure cleaned "low white" gutta-percha (preferably less rather than more) .....	9
"Crumb" or ground good old vulcanized india rubber.....	34
Hardwood veneer dust .....	5
Sulphur .....	6½
Zinc oxide (or zinc dust) .....	3¼
Flocking, or the cut fiber of cotton textile fabrics.....	3¼
Total .....	100

## COMPOUND NO. II.

Pure cleaned tough gutta-percha .....	8½
Pure cleaned balata or selected gutta-percha.....	8½
Pure cleaned "low white" gutta-percha .....	24
"Crumb" or ground good old vulcanized india rubber.....	33
Hard ground veneer dust .....	5
French chalk, powdered .....	6
Sulphur .....	6
Zinc oxide (or zinc dust) .....	3
Flocking, or the cut fiber of cotton textile fabrics.....	3
Alum, ground .....	3
Total .....	100

Another compound patented by Mr. Dick embraced the use of low grade African and Borneo rubbers, which, after cleansing, were mixed with gutta-percha, while still moist, in hot water. After the mixing the compound is treated under a moist heat, where the temperature is 212 degrees to 240 degrees F., the result being a tough, plastic fibrous dough. This compound is then, so the inventor claims, equal to any service for which the gutta-percha and balata compounds are used. An important property in this compound is the shrinking quality which gutta-percha possesses, while its power of cohesion rendered it especially valuable for insulating wires.

Shepard mixed gutta-percha with sulphur, exposed it to a heat varying from 300 degrees to 350 degrees F., admitting



hot air, then combined it with sulphur and earthy matters. It was then vulcanized by Parkes's cold-curing process.

Parkes dissolved balata and mixed it with 5 per cent. of chloride of sulphur, diluted with mineral naphtha. Gun cotton was also dissolved to a pasty mass, in naphtha distilled with chloride of calcium, and the two solutions were combined, forming a soft, flexible compound.

Childs vulcanized gutta-percha by mixing it with sulphur and placing it in a vulcanizer containing hydrated lime, and then turning on heat sufficient to obtain enough steam from the lime to do the curing.

Duvivier and Chaudet treated gutta-percha with bromide of sulphur or chloride of sulphur, making it more elastic and less liable to be acted on by heat or cold. When acid vapors were formed during the operation, carbonate of sodium was mixed with the solution.

Rostaing made gutta-percha hard and unalterable by treating it, after cleansing, with caustic soda, which was thoroughly washed out, after which it was combined with silicate of magnesia and treated with tannin, catechu, and other astringent matter.

Keene cured gutta-percha articles by exposing them to the fumes of sulphur or immersing them in a bath of melted sulphur.

Charles Hancock treated gutta-percha in a bath of boiling water in which was carbonate of potash, or muriate of lime, leaving it for an hour, and then mixing it with lead, glue, and bitumen. His claim was that this treatment hardened the gutta-percha, rendered it better adapted for bearing friction, and less likely to be oxidized. He also cured gutta-percha by mixing with it sulphur sulphides or orpiment, and applying heat. He gave as a compound for vulcanizing gutta-percha 48 parts gutta-percha, 6 parts golden antimony sulphuret, and 1 part sulphur, the compound to be boiled under pressure.

Emory Rider mixed gutta-percha with oxide of lead, heated it in open steam heat until the oily matters were expelled, then mixed it with hyposulphite of lead and cured it.

Lucas prepared a printing roll of gutta-percha, first im-

mersing the gutta-percha in nitric acid, and then placing it for an hour in a solution of carbonate of soda, thus producing a tougher wearing surface.

Barlow and Forster mixed gutta-percha with kauri gum and milk of sulphur for a cable coating.

Macintosh immersed gutta-percha in concentrated sulphuric acid for a number of seconds to harden the surface. He also mixed gutta-percha with gun cotton, curing with sulphuric acid, claiming that the resultant compound was not likely to be affected by the heat of tropical climates.

#### TYPICAL GUTTA-PERCHA CEMENT COMPOUNDS.

1.—For joining wood: gutta-percha, 11 pounds; shellac, 3 pounds; Venice turpentine, 5 pounds; pitch, 1 pound.

2.—For uniting metals, glass, stone, and earthenware: gutta-percha, 45 pounds; shellac, 20 pounds; gum mastic, 5 pounds; oxide of lead,  $\frac{1}{2}$  pound; storax, 3 pounds; Venice turpentine,  $26\frac{1}{2}$  pounds.

3.—For cementing leather: gutta-percha, 4 ounces; bisulphide of carbon, 20 ounces; asphaltum, 1 ounce; common resin, 1 ounce.

4.—Gutta-percha glue: gutta-percha, 1 pound; rosin, 1 pound; litharge, 1 ounce; powdered glass, *quantum sufficit*.

5.—Shoemaker's wax: melt gutta-percha, 20 ounces; add pitch, 58 ounces; soap, 5 ounces; rosin, 6 ounces; beeswax, 5 ounces; palm oil, 1 ounce; tallow, 5 ounces.

6.—For preserving metals and other surfaces: coal tar, 20 pounds; gutta-percha, 5 pounds; minium, 6 pounds; white lead, 7 pounds; pitch, 10 pounds; resin, 10 pounds; spirit turpentine, 4 pounds; sulphur, 38 pounds.

7.—General cement: Make a solution of balata of 5 ounces in  $\frac{1}{4}$  gallon naphtha, and another of gutta-percha 5 ounces in  $\frac{1}{4}$  gallon naphtha. Combine the two solutions and add 13 ounces resin or pitch and stir and mix thoroughly.

"Gentsch's gutta-percha" is a widely used substitute for gutta-percha, made in general as follows: the ingredients used are mineral wax, tar, resin and rubber. The process is thus described by a scientist who visited the English factory. A mixture of resin, wax, and tar was thrown into a kneading machine, steam being applied from below to keep the tem-

perature at the proper point. Twenty minutes later, the mass having been kneaded meanwhile, the steam was turned off and the rubber (cut into small pieces) added, being fed in slowly to prevent jamming of the knives of the kneading machine. The machine was stopped from time to time to test the condition of the mass, and at the end of three hours the solution of the rubber was found to be complete and the mass was removed from the machine and passed between rollers, coming out in slabs  $\frac{1}{4}$  inch thick—the finished material.

#### THE ANALYSIS OF GUTTA-PERCHA.

THIS of course refers to the analysis for the crude gum, and, to have the analysis complete, it should cover the amount of water present, the amount of foreign matters and impurities, the amount of ash, the amount of pure gutta, and the amount of resins.

The water is easily determined by heating a known weight from the sample at a temperature ranging from 212 degrees to 230 degrees F., the loss in weight being the amount of water present. This is a common process in chemical analysis. In the case of gutta-percha, it must be varied, as the sample is liable to oxidize even under examination, causing an increase of weight. This is overcome by conducting the heating in a slow current of nitrogen, or carbonic acid gas.

J. A. Montpellier devised an apparatus for this, which consisted of a special retort with a large opening which he used as a vapor bath and having a tubulure at its side. It is closed by a large cork, in which there are two holes, one for the tube which is to introduce the gas, and the other for the thermometer. The sample to be dried is placed in a crucible of porcelain or platinum suspended within the retort. As the water evaporates it is borne by the current of gas through a tube inserted in the side tubulure, and into U-shaped tubes, containing sulphuric pumice, which retain it. Further on the U-tubes are connected with a Liebig tube with five bulbs containing pure sulphuric acid to prevent the entrance of moist air after the apparatus cools, a further use being to make it possible to regulate the speed of the current of gas.

The retort is immersed in an oil bath heated by a Bunsen burner. If carbonic acid be used it is obtained by the action of

hydrochloric acid on marble chips produced in a Kipp apparatus followed by wash flasks, the first of which contains potassium bicarbonate in solution, which is intended to stop the passage of any hydrochloric acid, and the second containing sulphuric acid at 150 degrees to thoroughly dry the gas. To be absolutely sure that this gas is dry a desiccator filled with sulphuric pumice is placed between the retort and the second wash flask. The operation of drying one gram with this apparatus takes 6 to 7 hours. The determination of the amount of impurities, which comes next, may be effected very easily, by using M. J. Jean's exhaust apparatus. A small part of the sample, from one-half a gram to a gram, is weighed, cut into small fragments, put in a filter, the weight of which is known, which in turn is placed in a platinum cone. This cone is then put in the extension of the apparatus; this extension communicates by two tubes with the retort containing pure chloroform. A condenser, in which a current of cold water constantly circulates in order to condense the chloroform vapor, is placed at the upper part of the extension.

The retort rests on a sand-bath, very gently heated by a Bunsen burner. Under the influence of the slight heat the chloroform evaporates, passes through one of the tubes, and drops on the filter containing the gutta-percha, which it gradually dissolves. The solution, passing through the filter, then drips into the retort through the second tube.

All the impurities remaining in the filter, it is sufficient to dry and weigh the filter to get the weight of the foreign matters. The drying should be done in the apparatus used in determining the amount of water.

The next process is the determination of the amount of ash. In gutta-percha this is always very small, as mineral matter is almost entirely absent from it, the quantity never exceeding one-half of 1 per cent. The amount of ash is determined by burning in a capsule of platinum a known weight of gutta.

The fourth step is the determination of the amount of pure gutta, and of the resins. Both fluavile and albane are soluble in absolute alcohol at the boiling point, and as pure gutta is insoluble in it, this is a very ready means of separa-

tion. The sample to be examined is cut in little bits, put in a platinum basket, which is pierced with holes, and hung in a retort containing the alcohol. This retort is heated with a sand-bath or water bath, the vapor of the alcohol passing through a Liebig condenser and returning to the retort. The boiling is continued for 5 or 6 hours, with the basket immersed in alcohol. It is then raised above the liquid, and the boiling continued for 5 or 6 hours more. The latter part of the process removes the last traces of resin.

The boiling operation being completed, the pure gutta, together with the impurities, remains on the filter. There remains then the drying of the filter in the apparatus used in determining the amount of water and the weighing of it. The loss of weight shown by the gutta-percha corresponds to the amount of resins increased by the weight of the water. Subtracting that weight, already determined, the weight of the resins remains.

Wilton G. Berry, Ph.B., is the author of a monograph on the analysis of gutta-percha resins, the basis of which was a paper read before the Society of Chemical Industry. In it he dealt with the comparative quantitative analysis by treatment of the previously dried material with acetone, alcoholic-potash, and petroleum ether, and extraction of the resins in a uniform manner with boiling absolute alcohol, and the separation of the extracted resins into their component resins, soluble and insoluble in cold absolute alcohol.

The object was the determination of—

Saponification value,  
Acid value,  
Ether value,  
Iodine value,  
Acetyle value,  
Methyl value,  
Melting point, solubility, etc.

—of the individual resins, hoping thus to establish a table of values whereby the resins of any given specimen may be identified and the identity of the parent gum thus established. The gums thus far experimented on are a few specimens each of gutta-percha, chicle, Almeidina, tuno, jelutong (Pontianak), balata, and *Payena* species.

It has been found thus far that the resins from several



specimens of the same gum have practically the same constants and characteristics, and that the resins from the different species of gums have different constants and characteristics—in some widely different, and in the cases of the gums above cited sufficiently differing to make identification of their parent gum an easy matter. From the gums so far examined it is hoped to establish the fact that the combined evidence of the constants and characteristics of the resins, together with the character of the accompanying hydrocarbons, will show that each species of gum varies from each other sufficiently to make differentiation of unnamed specimens complete, and to establish the fact that every specimen of the same species of gum is alike in the characteristics quoted.

#### RÉSUMÉ OF ANALYTICAL WORK.

*Gutta-percha*—Resins, soft, pasty, yellow.

*Chicle*—Resins hard, grayish yellow, brittle.

*Tuno*—Resins hard, dark yellow, brittle.

*Almeidina*—Resins hard, brittle, yellow.

*Jelutong*—Resins soft, brittle, yellow.

*Balata*—Resins turbid liquid, yellow.

*Payena*—Resins similar to chicle resins.

	Saponification Value	Acid Value
*Gutta-percha resins .....	78.5	5
*Gutta-percha (albane) .....	83.5	—
*Gutta-percha (fluavile) .....	71.45	—
*Chicle resins .....	103.1	Trace
Chicle (resin A) .....	129.0	Trace
Chicle (resin B) .....	100.8	Trace
†Tuno resins .....	77.3	5.6
†Jelutong .....	77.5	Trace
Almeidina .....	50.4	11.0
Balata .....	69.2	Trace
†Payena species .....	103.7	Trace

\*Average of 4 specimens. †Average of 2 specimens.

While the saponification values of gutta-percha, tuno, and jelutong resins respectively are almost identical, their separation into component resins corresponding to albane and fluavile of gutta-percha gives entirely different results from the latter and from each other. The resins of chicle and *Payena* differ as widely and the accompanying hydrocarbons are quite different.

Analyses of common gutta-percha, by Edouard Heckel and Fr. Schlagdenhauffen:

Gutta .....	75 to 82
Albane .....	19 to 14
Fluavile .....	6 to 4

Total .....	100	100
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Analysis by Payen:

Gutta .....	78 to 82
Albane .....	16 to 14
Fluavile .....	6 to 4

Total .....	100	100
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Gutta-percha is made of a mixture of hydrocarbons, and there is usually present a certain amount of oxygen. According to Granville H. Sharpe, F.C.S., its ultimate composition is:

Carbon .....	86.36
Hydrogen .....	12.15
Oxygen .....	1.49

Total .....	100.
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[Specific gravity, 0.96285 to 0.99923.]

The primary analysis of gutta-percha by Sharpe is:

Hydrocarbon .....	79.70
Resin .....	15.10
Wood fiber .....	2.18
Water .....	2.50
Ash .....	0.52

Total .....	100.
-------------	------

Obach gives the following average results from a large number of analyses of each of twelve leading brands or sorts of gutta-percha:

	Gutta	Resin	Dirt	Water
Pahang .....	78.1	19.2	1.5	1.2
Bandjer red .....	67.0	30.2	1.5	1.3
Bulongan red .....	68.6	29.0	1.4	1.0
Bagan .....	57.5	40.9	1.0	0.6
Goolie red soondie .....	55.2	42.9	1.2	0.7
Serapong .....	56.2	42.4	0.9	0.2
Bulongan white .....	52.2	45.4	1.5	0.9
Mixed white .....	49.8	47.4	1.1	1.7
Bandjer white .....	51.8	44.1	1.8	2.3
Sarawak mixed .....	55.6	40.9	1.8	1.7
Padang reboiled .....	50.3	45.8	2.0	1.9
Banca reboiled .....	46.8	51.1	1.1	1.0

Another series of analyses by Obach relate to the constituents of the resins in gutta-percha, as follows:

	Albane	Fluavile
Carbon .....	78.76	80.79
Hydrogen .....	10.58	11.00
Oxygen .....	10.46	8.21
Total .....	100.	100.

## BALATA.

BALATA is the gum of the "bully" or "bullet" tree—the *Minusops balata*—found in British and Dutch Guiana, and in Venezuela. It is marketed in two forms, "block" and "sheets." The sheet is usually worth about 30 per cent. more than the block balata. The sheet is used for belt covering, while the block is more used in compounding. Balata is usually reddish gray, though sometimes brown. The dried sheet milk or sheet product usually contains 39 per cent. gutta and 37 per cent. rosin; while the boiled or block contains 51 per cent. gutta and 48 per cent. rosin. The sheet shrinks from 10 to 20 per cent. while the block shrinks from 20 to 30 per cent.

The balata tree may be tapped when 5 inches in diameter. If tapped too deep, the tannin sap injures the product, and the wound is slow to heal. The outer bark is removed before tapping. The milk runs for about three hours, and a tree will generally yield about 3.6 liters of milk, or  $1\frac{1}{2}$  to 2 kilos of balata. It usually requires about two weeks for the milk to dry.

In character this gum occupies a position between india rubber and gutta-percha, combining in a degree the elasticity of one with the ductility of the other, and freely softening and becoming plastic and easily molded in hot water. Balata is dried ordinarily by evaporation. A more rapid coagulation is effected by the use of spirits of wine. Alum is sometimes used to coagulate, but is not very satisfactory. The gum is sometimes mixed during the gathering with the milk that produces gum known as touchpong and barta-balli. It is used principally in the manufacture of belting and for insulation work. It has been utilized also for golf balls and as a substitute for rubber in dress shields.

# INDEX

ABBA rubber .....	33
<i>Abies balsamea</i> .....	158
Abyssinian gutta .....	33
<i>Acacia</i> .....	155
Acacia gum .....	153
Accelerators .....	80, 82
Amino compounds .....	83, 197
Accelerene .....	83
Formin .....	84
Hexamethylene amine .....	84
Hexamethylene tetra- mine .....	84
Miscellaneous .....	84
Paranitroso dimethyl- aniline .....	83
Para-phenylenediamine .....	84
Tetramethylene dia- mine .....	84
Ammonium compounds .....	82
Aldehyde ammonia ..	82
Ammonium borate ...	82
Quaternary ammo- nium bases .....	83
Aniline .....	81
Carbon bisulphide addi- tion products .....	82
with aniline .....	82
with $\beta\beta$ dimethyl $\alpha$ - methyl trimethylene amine .....	82
with dimethylaniline ..	82
with dimethylamine ..	82
with tetrahydropyrrole ..	82
Miscellaneous .....	86
Accelema! .....	87
Albumen .....	86
Annex .....	87
Anthraquinone .....	86
Antipyrine .....	86
Anvico .....	87
Caustic alkali and gly- cerol .....	87
Dry aniline .....	87
Duplex .....	87
Excellerex .....	88
Formanilide .....	86
Magnesia .....	86
Naphthylamine .....	86
Paradin .....	88
Quicklime .....	87
Tensilite .....	88

## Accelerators—Continued.

### Miscellaneous—Continued

Thioformanilide .....	86
Urea .....	86
Velocite .....	88
Velosan .....	88
Vitaminex .....	88
Vulcacit .....	88
M. C. C. .....	88
Piperidine derivatives..	84
Aminopentane .....	84
Methyl piperidine ....	85
Piperidine .....	85
Quinoline and derivatives ..	85
Hydroxy quinoline ..	86
Oxiquinoline .....	85
Oxiquinoline sulphide. ..	85
Oxyquinoline sulphonic acid .....	85
Quinoline .....	85
Quinoline sulphate ...	85
Quinosol .....	85
Accra rubber .....	20
Acetic acid .....	48, 194
Acetone .....	230
<i>Achras sapota</i> .....	35
Acid, Acetic .....	48, 194
Boracic .....	199
Carbolic .....	199
Chromic .....	200
Citric .....	200
Formic .....	48, 201
Hydrochloric .....	201
Mimo-tannic .....	202
Muriatic .....	202
Nitric .....	202
Oleic .....	203
Oxalic .....	203
Salicylic .....	206
Sulphuric .....	210
Tannic .....	211
Tartaric .....	211
Tungstic .....	212
Acid cure .....	54
Acids, alkalies and derivatives ..	194
Acroides gum .....	153
Action of metals on rubber .....	262
Foden on .....	262
Morgan on .....	263
Schidrowitz on .....	263

- Adamanta ..... 119  
     resin ..... 154  
 Adam's process for uniting rubber to metals ..... 260  
 Addah Niggers rubber ..... 20  
 Adhesor ..... 119  
 African rubbers ..... 17  
     rubber sources ..... 9, 17  
 Agalmatolite ..... 89  
 Air brake and signal hose tests.. 343  
 Alcohol ..... 48, 230  
     Denatured ..... 231  
 Alexander's reclaiming process. 295  
 Alexite ..... 141  
 Algin gum ..... 119  
 Allard's fireproof felt ..... 255  
 Almeida rubber ..... 33  
*Alstonia plumosa* ..... 41  
 Alum ..... 48, 194  
 Alumina ..... 89  
 Aluminite ..... 89  
 Aluminum flake ..... 89  
     lanolate ..... 213  
     oxide ..... 89  
     sulphate ..... 195  
 Alundum ..... 89  
 Alying's rubber cure ..... 58  
 Amazonian resin rubbers ..... 34  
 Amber ..... 154  
     Burmite ..... 158  
     resin substitute ..... 119  
 Ambriz rubber ..... 23  
 Ambroin ..... 141  
 American process zinc oxide .... 190  
 American showerproofing compounds ..... 252  
 American Society For Testing Materials; methods of analysis .... 321  
 Amianthus ..... 91  
 Ammonia ..... 196  
 Ammonium carbonate ..... 196  
     chloride ..... 197  
     muriate ..... 197  
     tungstate ..... 197  
 Amole juice ..... 48  
 Amorphous sulphur ..... 63  
 Amphiboline ..... 89, 255  
 Analyses of oil substitutes (table) 118  
 Anderson's reclaiming process.. 295  
 Angola rubbers ..... 23  
 Angostura rubber ..... 13  
 Anhydrite ..... 90  
 Aniline ..... 197  
     colors for rubber..... 177  
 Anime ..... 155  
 Ant wax ..... 40  
 Anthracene ..... 239  
 Antimony ..... 90  
     crimson sulphide ..... 184  
     golden sulphide ..... 191  
     iodide ..... 198  
     oxide ..... 90  
     red sulphuret ..... 66  
 Antipolo gum ..... 34  
*Apocynaceæ* ..... 7  
 Arabic Gum ..... 155  
 Argillaceous red shale ..... 90  
 Arkosite ..... 155  
 Armalac ..... 141  
 Arsenate, Potassium ..... 204  
 Arsenic ..... 90  
     yellow ..... 191  
*Artemisia absinthium* ..... 227  
*Artocarpaceæ* ..... 7  
*Artocarpus incisa* ..... 34  
     *integrifolia* ..... 35  
 Aruwimi rubber ..... 22  
 Asbestic ..... 91  
 Asbestine ..... 91  
 Asbestonit ..... 120  
 Asbestos ..... 91  
     Analysis of ..... 92  
*Asclepiadaceæ* ..... 7  
 Asphalt ..... 155  
     Artificial ..... 156  
     French ..... 162  
     Lithro-carbon ..... 165  
     Manjak ..... 166  
     Mineral india rubber ... 166  
     Retin ..... 170  
     Trinidad ..... 174  
 Assam rubber ..... 25  
     white ..... 38  
 Assinee rubber ..... 20  
*Astragalus gummifera* ..... 174  
 Astrictum ..... 120  
*Attalea excelsa* ..... 45  
 Atmido ..... 92  
 Atmoid ..... 92  
 Attoaboa rubber ..... 20  
 Aureolin ..... 192  
 Aylsworth's Condensite ..... 144  
 Axim rubber ..... 20  
 A. R. D. Gum ..... 119  
 BAKA gum ..... 34  
 Bakelite ..... 142  
 Balata ..... 398  
     analyses of ..... 383  
 Balenite ..... 142  
 Ball, African ..... 18



- |  |          |                                      |          |
|--|----------|--------------------------------------|----------|
| Balsam .....                                     | 156      | Birch-bark tar .....                 | 157      |
| Canada .....                                     | 158      | Biscuits, African .....              | 19       |
| of storax .....                                  | 156      | Bisulphate, Potassium .....          | 204      |
| of sulphur .....                                 | 156      | Bisulphide, Carbon .....             | 234      |
| Tolu .....                                       | 174      | substitute, Carbon .....             | 234      |
| Balsams in rubber compounding .....              | 153      | Bisulphite, Sodium .....             | 208      |
| Banana rubber .....                              | 34       | Bitumen .....                        | 157      |
| Bangui rubber .....                              | 22, 378  | Auvergne .....                       | 157      |
| Bannigan rubber cure .....                       | 57       | Black, Antimony .....                | 93       |
| Barabarja rubber .....                           | 24       | Bone .....                           | 179      |
| <i>Barberis vulgaris</i> .....                   | 192      | Carbon .....                         | 179      |
| Barberry yellow .....                            | 192      | Gas .....                            | 179      |
| Barium carbonate .....                           | 92, 95   | Graphite .....                       | 179      |
| chloride .....                                   | 198      | Hydrocarbon .....                    | 179      |
| sulphide .....                                   | 64       | Hypo .....                           | 63, 178  |
| white .....                                      | 186      | Jet .....                            | 179      |
| Barlow and Forster's gutta-percha compound ..... | 392      | Lamp .....                           | 179      |
| Barta-Balli gum .....                            | 34       | lead .....                           | 93       |
| Barytes .....                                    | 92       | Paris .....                          | 180      |
| Baschnagel's reclaiming process .....            | 293      | pigments for rubber .....            | 178      |
| Basle's reclaiming process .....                 | 296      | pitch .....                          | 158      |
| Bassam rubber .....                              | 19       | Satin gloss .....                    | 180      |
| <i>Bassia Parkii</i> .....                       | 37       | Blanc fixe .....                     | 93       |
| Basofo .....                                     | 93       | Blandite .....                       | 120      |
| Batanga ball rubber .....                        | 21       | Blandy's patent substitute .....     | 120      |
| Bathurst rubber .....                            | 19       | Bleaching powder .....               | 198      |
| Bayin rubber .....                               | 20       | Bleached oils .....                  | 213      |
| Beadle and Stevens, analyses of                  |          | Blue, Chinese .....                  | 181      |
| <i>Hevea latex</i> .....                         | 44       | Chrome .....                         | 181      |
| bleaching of crude rubber .....                  | 53       | Cobalt .....                         | 181      |
| mechanical impurities in                         |          | Indigo .....                         | 181      |
| crude rubber .....                               | 309      | lead .....                           | 93       |
| Beckton White .....                              | 187      | Molybdenum .....                     | 181      |
| Beeswax .....                                    | 156      | pigments for rubber .....            | 180      |
| Beira rubber .....                               | 35       | Prussian .....                       | 181      |
| Belgian Congo rubber .....                       | 22       | Saxon .....                          | 181      |
| Belledin's process for leather                   |          | Smalts .....                         | 182      |
| impregnation .....                               | 120      | Thenard's .....                      | 182      |
| Benguela rubber .....                            | 23       | Ultramarine .....                    | 182      |
| Benin ball rubber .....                          | 21       | Yale .....                           | 183      |
| Benton, preservation of rubber                   |          | Bolivian rubber .....                | 12       |
| goods .....                                      | 258      | Bone ash .....                       | 94       |
| Benzene .....                                    | 232, 240 | black .....                          | 94       |
| Benzine .....                                    | 239, 240 | naphtha .....                        | 237      |
| Benzoin .....                                    | 157      | Book gutta .....                     | 26       |
| Benzol .....                                     | 232      | Boots and shoes, Compounds for ..... | 360      |
| Benzole .....                                    | 232      | Dry heat cure of .....               | 358      |
| Bernstein, vulcanization by ultra                |          | Manufacture of .....                 | 357      |
| violet rays .....                                | 61, 62   | Pressure cure of .....               | 359      |
| Berry, analysis of gutta-percha                  |          | Varnish for .....                    | 361      |
| resins .....                                     | 395      | Boracic acid .....                   | 199      |
| Besk .....                                       | 26       | Borate, Zinc .....                   | 187      |
| Beta separator .....                             | 50       | Borax .....                          | 199, 207 |
| Betite .....                                     | 142      | Borcherdt's compound .....           | 120      |
| Beverly Rubber Works .....                       | 293      | Borneo rubber .....                  | 25       |
| Beylikgy's reclaiming process .....              | 295      | No. 3 .....                          | 38       |
| Biborate, Sodium .....                           | 207      | <i>Borracha</i> .....                | 14       |
| Bichromate, Potassium .....                      | 204      | Bosanga rubber .....                 | 48       |
|  |          | Botany Bay gum .....                 | 153      |

- Bougival white ..... 187  
 Bourn's reclaiming process ..... 294  
*Brassica campestris* ..... 225  
 Brierly's patent artificial elater-  
     ite ..... 120  
 Brimmer's reclaiming process .. 296  
 British gum ..... 158  
 Brittleness in rubber goods .... 257  
 Brixey's Kerite formula ..... 128  
 Bromine ..... 64  
 Brooksite ..... 143  
*Brosimum galactodendron* ..... 37  
 Brown pigments for rubber ..... 184  
 Brown's hard rubber substitute.. 143  
 Bucaramanguina ..... 94  
 Buki rubber ..... 23  
 "Bullet" tree gum ..... 398  
 "Bully" tree gum ..... 398  
 Bumba rubber ..... 23  
 Burgundy pitch ..... 158  
 Burmite amber ..... 158  
 Burnt hypo ..... 63  
     umber ..... 94  
 Bussira rubber ..... 22  
 Butanes, Rubbers from ..... 272  
 Button lac ..... 158  
 Buttons, African ..... 19  
*Butyrospermum Parkii* ..... 38
- CADMIUM yellow ..... 192  
 Cadoret's resinolines ..... 134  
 Calamine ..... 94, 187  
 Calcium carbonate ..... 94  
     chloride ..... 199  
     oxalate ..... 199  
     oxide ..... 199  
     phosphate ..... 94  
     sulphate ..... 95  
     sulphide ..... 199  
     white ..... 95  
 Calculation of analyses ..... 320, 321  
 Calendering rubber ..... 353  
 Calomel ..... 95  
*Calonyction speciosum* ..... 48  
*Calotropis gigantea* ..... 40  
 Cameroons rubber ..... 21  
 Cameta rubber ..... 11  
 Campbell and Cushman's punc-  
     ture fluid ..... 266  
 Campbell's Endurite ..... 124  
 Camphene ..... 233  
 Camphor ..... 158, 233  
     Oil of ..... 214  
 Canada balsam ..... 158  
 Candelitta wax ..... 159  
 Candle tar ..... 159
- Canoe gums ..... 35  
 Caoutchene ..... 121  
 Caoutchite ..... 121  
 Caoutchouc aluta ..... 143  
     oil ..... 214  
 Caoutchoucine ..... 234, 376  
 Cape Coast rubber ..... 20  
 Carbolic acid ..... 199  
 Carbon bisulphide ..... 234  
     bisulphide substitute ... 235  
     black ..... 179  
     tetrachloride ..... 235, 244  
 Carbonaceous clay ..... 95  
 Carbonate, Barium ..... 95  
     Potassium ..... 204  
     Sodium ..... 208  
 Carbo-nite ..... 143  
 Carburet of iron ..... 95  
 Carn gum ..... 159  
 Carnauba wax ..... 159  
 Carrol gum ..... 121  
 Carr's patent cereal gum ..... 121  
 Carsel yellow ..... 102  
 Cartagena rubber ..... 15  
 Casein ..... 159  
 Caspari crude rubber valuation  
     methods ..... 308  
     tetrabromide method for  
         determining rubber. 310  
*Castilloa elastica* ..... 9  
     *tunu* ..... 43  
     *Ulei* ..... 9  
 Castilloa plantation rubber ... 31  
 Castor oil ..... 214  
 Catechu ..... 200  
 Cativo gum ..... 35  
 Cattimandu gum ..... 35  
 Cauchin rubber ..... 39  
 Caucho rubber ..... 13, 14  
 Caulbry's rubber cure ..... 60  
 Caustic potash ..... 205  
     soda ..... 209  
 Caviana rubber ..... 11  
 Ceara rubber ..... 16  
     plantation rubber ..... 31  
 Cellit ..... 143  
 Cellulith ..... 143  
 Celluloid ..... 143  
 Cellulose ..... 143  
 Cement, Gutta-percha ..... 392  
     Portland ..... 108  
     Rubber ..... 372  
 Central American rubber ... 14, 31  
     plantation rubber ..... 31  
 Cellazote ..... 267  
 Ceramyl ..... 159  
 Cerasin ..... 160  
*Ceratonia siliqua* ..... 174

- Cereal rubber ..... 121  
 Ce-re-gum ..... 144  
 Ceylon rubber ..... 29  
 Chalk ..... 95, 113  
 Charcoal, Animal ..... 96  
     Vegetable ..... 96  
 Charlton white ..... 187  
 Chatterton's compound ..... 144, 387  
 Chautard's reclaiming process.. 296  
 Cherry gum ..... 160  
 Chicle gum ..... 35  
     substitute ..... 121  
 Child's gutta-percha compound 391  
 China clay ..... 96  
 Chinese blue ..... 181  
     white ..... 187, 190  
 Chloride of lime ..... 198, 200  
     Propylene ..... 244  
     Sodium ..... 208  
     Sulphur ..... 65  
     Zinc ..... 212  
 Chlorine ..... 64  
 Chloroform ..... 236  
 Cholesterin ..... 214  
 Christia gum ..... 121  
 Chrome blue ..... 181  
     green ..... 183  
     yellow ..... 192  
 Chromic acid ..... 200  
 Chute's rubber resin solvent ... 236  
 Citric acid ..... 200  
 Clapp's reclaiming process ..... 293  
 Classification of gutta-percha.. 378  
 Clift's reclaiming process ..... 296  
 Clothing, proofing and carriage  
     cloth, Compounds for 364  
     Manufacture of ..... 364  
 Coagulation of rubber latex.. 44, 45  
     by drying ..... 46  
     by smoking ..... 45  
     Chemical ..... 46  
     Electric ..... 52  
     Frank-Markwald's  
         process for ..... 51  
     Leva process for ..... 46  
     Machines for ..... 50  
     Mechanical ..... 47  
     Purpose of ..... 45  
 Coal, Powdered ..... 109  
     naphtha ..... 239  
     tar ..... 160  
 Coalite pitch ..... 160  
 Coarse Para Rubber ..... 11  
 Cobalt blue ..... 181  
     yellow ..... 192  
*Coccus lacca* ..... 171  
 Coconut water ..... 48  
 Cod-liver oil ..... 214  
 Coefficient of vulcanization and  
     state of cure..... 347  
 Cohuru's waterproof compound.. 255  
 Colcothar ..... 184  
 Cold cure ..... 54  
 Colophane ..... 160  
 Colophony ..... 160  
 Colors, Aniline ..... 177  
 Colombian rubber ..... 15  
 Colza oil ..... 215, 225  
 Combined sulphur, Dr. Stevens  
     and Dr. De Vries  
     on ..... 347  
 Compo ..... 96  
*Composita* ..... 7  
 Composition of rubber ..... 8  
 Compound, Barlow and Forster's 392  
     Chatterton's ..... 144, 387  
     Child's ..... 391  
     Cooley's ..... 388  
     Dick's ..... 389, 390  
     Duncan's ..... 388  
     Duvivier and Chaudet's.. 391  
     Forster's ..... 388  
     Gaullie's ..... 388  
     Godefroy's ..... 389  
     Hancock's, Charles.. 388, 391  
     Hutchinson's ..... 388  
     Keene's ..... 391  
     Lucas's ..... 391  
     Macintosh's ..... 388, 392  
     Parkes's ..... 391  
     Rider's, Emory ..... 391  
     Rostaing's ..... 391  
     Shepard's ..... 390  
     Smith's, Willoughby 152, 387  
     Sorel's ..... 151  
     Spill's ..... 389  
     Wray's, Leonard ... 152, 387  
 Compounds, boot and shoe, Rub-  
     ber ..... 360  
 Cement, Rubber ..... 372  
     clothing and carriage  
         cloth, Rubber ..... 364  
 Dental and stamp gum.. 373  
 Druggists', stationers'  
     and surgical rub-  
         ber goods ..... 363  
 Gas-tight rubber ... 261, 262  
 Gutta-percha ..... 387  
 Hard rubber ..... 371  
 insulation, Rubber ..... 369  
 Kiel's hard rubber ..... 148  
 Mechanical rubber goods 355  
 Molded rubber goods ... 370  
 Notion-trade rubber .... 374  
 plaster, Adhesive ..... 375  
 tire, Rubber ..... 367

- Compounding, Reasons for rubber 89  
 Waxes in rubber ..... 153  
 Conakry rubber ..... 19  
 Con-current rubber ..... 122  
 Condensite ..... 144  
 Congo Free State rubbers ..... 22  
 plantation rubber ..... 31  
 Consolidated oil ..... 215  
 Cooley's artificial leather ...102, 156  
 gutta-percha compound 388  
 Coorongite .....36, 160  
 Copal ..... 160  
 Copper sulphate ..... 200  
 Coralite ..... 145  
 Corimite ..... 145  
 Cork ..... 97  
 leather ..... 122  
 Corkaline ..... 122  
 Corn oil ..... 215  
 substitute ..... 122  
 Cornite ..... 145  
 Cornwall clay ..... 97  
 Corundum ..... 97  
 "Coruscus" finish ..... 98  
*Corypha cerifera* ..... 159  
*Costus afer* ..... 48  
 Cottonseed oil ..... 215  
*Couma utilis* ..... 37  
 Coutinho's machine ..... 50  
 Cow tree rubber ..... 37  
 Coyuntla juice ..... 48  
 Cravenette process ..... 251  
 Cream of tartar .....201, 204  
 Creosote oil ..... 215  
*Croton draco* ..... 171  
 Crude rubber, Bleaching of.... 53  
 Cause of color in ..... 52  
 Mechanical and chemical  
 relationships of .. 345  
 Physical tests and analy-  
 ses of ..... 302  
 Shrinkage of ..... 263  
 African grades of..263, 264  
 Calculation of ..... 265  
 East Indian grades of 264  
 Para grades of ..... 263  
 Valuation of ..... 303  
 Classification in .... 306  
 Correlation of tests in 305  
 Estimation of moisture  
 in ..... 310  
 Estimation of rubber in 310  
 Fol's conclusions on.. 304  
 Form for reporting ... 310  
 Gorter's viscosity in-  
 dex in ..... 306  
 Mechanical impurities  
 in ..... 309  
 Moisture in ..... 310
- Crude rubber—*Continued*  
 Valuation of—*Continued*  
 Nitrogenous insoluble  
 matter in ..... 309  
 Practical considera-  
 tions on ..... 309  
 Schmitz method for. 309  
 Outline scheme for ... 304  
 Physical and mechani-  
 cal ..... 311  
 Adhesive tests in ... 311  
 Mechanical tests in.. 311  
 Viscosity tests in... 311  
 Vulcanization tests in 311  
 Secondary products  
 (rubber resins) in 308  
 Schidrowitz method of 307  
 Scientific method for.. 304  
 Tetra-bromide method  
 for rubber in ... 310  
 Washing loss in ..... 311  
 Cumai rubber ..... 37  
 Cumaka-balli ..... 35  
 Cutch .....200, 201  
 Cyanide, Potassium ..... 205  
 Cyco ..... 266
- DAFT's process for uniting rub-  
 ber to metal .... 261  
 Dammar ..... 161  
 Dankwerth's Russian substitute 122  
 Danin's machine ..... 50  
 Day's Kerite ..... 127  
 use of pipe clay..... 108  
 DaCosta's apparatus ..... 51  
 Denatured alcohol ..... 231  
 De Pont's substitute ..... 145  
 Dental and stamp gum, Com-  
 pounds for..... 373  
 Manufacture of ..... 373  
 Deodorization process .....116, 256  
 Bourne's ..... 256  
 Cattell's ..... 256  
 De la Granja's ..... 256  
 Freeley's ..... 256  
 Hancock's, Charles .... 256  
 Lavater and Tranter's.. 256  
 Traun Rubber Co.'s .... 257  
 Dermatine ..... 122  
 Derry's waterproof harness oil. 226  
 Dextrine ..... 161  
 Dextrose ..... 161  
 Diatite ..... 145  
 Diatomaceous earth ..... 98  
 Dichlor-ethylene ..... 236  
*Dichopsis elliptica* ..... 41  
*polyantha* ..... 379



- Dick's gutta-percha compounds 389, 390
- Dieffenbach's rubber cure ..... 56
- Dimethyl butanes, Rubbers from 272
- Dippel's oil ..... 236
- Divisions of rubber manufacture 354
- Doeblich's compound ..... 123
- Donaldson's electrolytic method for lead and zinc.. 332
- Doremus fireproofing process... 255
- Dow's inner-tube filler ..... 266
- Druggists', stationers' and surgical sundries, Compounds for ..... 361
- Manufacture of ..... 363
- Dry heat cure..... 54
- mixing ..... 359
- Rubber ..... 352
- Fillers in..... 89
- Unusual ..... 114
- Drying oil ..... 227
- Dull finish ..... 113, 221
- Dumas' canvas sail waterproofing ..... 255
- Duncan's gutta-percha compound 388
- Durant patent for bleaching gutta-percha ..... 236
- Durate ..... 123
- Durvez's reclaiming process... 296
- Dutch Congo ball rubber ..... 22
- liquid ..... 237
- pink ..... 192
- Duvivier and Chaudet's gutta-percha compound. 391
- Duvivier's gutta-percha compound ..... 107
- Dyeing rubber ..... 247
- Frankenburg's aniline lakes for ..... 249
- Hoffer's method for... 247
- Parkes' formulæ for... 247
- Dyera costulata* ..... 26
- EARTH wax ..... 161
- East Africa rubbers ..... 23
- East Indian rubber ..... 25
- Sources of ..... 9
- Eaton, B. J. and Grantham J., on optimum cure ..71, 73
- Eaton's, A. K., rubber cure..... 56
- Ebner's patent A. R. D. Gum... 119
- Ebonitine ..... 145
- Eckstein's Hyaline ..... 147
- Ekert's high pressure composition 123
- Elasteine ..... 123
- Elastes ..... 266
- Elastic glue ..... 123, 161
- Elasticite ..... 123
- Elastite ..... 123
- Elaterite ..... 130, 161
- Artificial ..... 119
- Elateron hydrocarbon ..... 131
- Electric coagulation process .... 52
- curing process ..... 63
- finish ..... 98
- properties of gutta-percha ..... 385
- Electroplating on rubber, Good-year's method of.. 248
- Electrose ..... 145
- Elemi ..... 162
- Elmer's rubber cure ..... 59
- Elworthy's process for preserving rubber goods .... 258
- Emarex mineral rubber..... 131
- Embossing rubber ..... 248
- Bourbridge method for.. 248
- Emery ..... 98
- Endurite ..... 124
- English show roofing compound ..... 253
- Entrefina* Para rubber ..... 10
- Enzymes in crude rubber..... 52
- Equateur rubber ..... 22
- Esbenite ..... 145
- Esmeralda rubber ..... 15
- Ether ..... 237
- Ethyline chloride ..... 237
- Eucaliptia ..... 215
- Eucalyptus globulus* ..... 216
- Eucalyptus oil ..... 216
- Eucommia ulmoides* ..... 42
- Euphorbia drageana* ..... 40
- fulva* ..... 41
- lactiflua* ..... 34
- rhipsaloides* ..... 34
- rubber ..... 34, 124
- tirucalli* ..... 34
- trigona* ..... 35
- Euphorbiaceæ* ..... 7
- Euphorbium, Gum ..... 162
- Eureka vulcanizing compound.. 63
- Everlastic ..... 266
- Eves's reclaiming process ..... 296
- FAGIOLI puncture fluid ..... 266
- Falke and Richard's rubber cure 56
- Faraday's analysis of latex... 266
- Fard's Spanish white ..... 188
- Farina ..... 98
- Faure's reclaiming process .... 294
- Fayolles' substitute ..... 124
- Feldspar ..... 99
- Fenton's artificial rubber ..... 124
- Fiber, Vulcanized ..... 152
- Fibrine-Christia gum ..... 124



- Fibrone ..... 146  
 Fichtelit ..... 162  
*Ficus elastica* ..... 9  
     *Indica* ..... 39  
     *obliqua* ..... 34  
     *Vogelii* ..... 9  
 Fig juice proofing ..... 124  
 Fillers in dry mixing ..... 89  
 Fine Para rubber ..... 10  
 Fire clay ..... 99  
     Allard's ..... 255  
     Doremus' ..... 255  
     Dumas' ..... 255  
     proofing ..... 255  
 Firmus ..... 124  
 Fish glue ..... 162  
     oil ..... 216  
 Flake, African ..... 18  
 Flint ..... 99  
     Liquor of ..... 202  
 Florence zinc ..... 190  
 Flour, Glass ..... 99  
     Phosphate ..... 99  
 Fluoride, Silicon ..... 206  
 Fluvia ..... 26  
 Fol on valuation of crude rubber ..... 304  
 Formic acid ..... 48, 201  
 Forster's gutta-percha compound ..... 388  
     showerproofing com-  
     pound ..... 254  
 Fossil farina ..... 99  
     flour ..... 99  
     meal ..... 99  
*Forsteronia gracilis* ..... 39  
*Fouquieria splendens* ..... 40  
 Frankenburg's aniline lakes ..... 249  
     non-inflammable rubber  
     solutions ..... 230  
     puncture fluid ..... 266  
 Frankincense ..... 162  
 Franklin substitute ..... 125  
 Frank-Marckwald's coagulation  
     process ..... 51  
 French asphalt ..... 162  
     chalk ..... 100  
     Congo rubber ..... 21  
     gutta-percha ..... 125  
     process zinc oxide ..... 190  
     reclaiming process ..... 296  
     talc ..... 111  
     West Africa rubbers ..... 19  
     wool grease ..... 216  
 Frost rubber ..... 125  
 Fuller's earth ..... 100  
 Fulton white ..... 188  
 Fumero of van den Kerckhove .. 51  
*Funtumia elastica* ..... 9  
     *kickxia* ..... 46  
 Fusel oil ..... 231  
 GABOON rubber ..... 21  
 Galalith ..... 146  
 Galipot ..... 171  
 Gambia niggers ..... 19  
 Gambie rubber ..... 19  
 Gamboge ..... 162, 193  
 Gambia ..... 26  
*Garicinia morella* ..... 193  
 Garnet lac ..... 163  
 Garnier's rubber cure ..... 60  
 Garrity and Avery's process for  
     uniting rubber to  
     metals ..... 260  
 Gas proofing ..... 261  
     Bousfield's ..... 261  
     Churrel's balloon ..... 261  
     compounds for ..... 261, 262  
     Pellen's ..... 261  
*Gascardia Madagascariensis* .... 40  
     *Perrieri* ..... 40  
 Gasoline ..... 237  
 Gaullie's gutta-percha compound ..... 388  
 Gelatine, Glugloss ..... 163  
 Genasco hydrocarbon ..... 131  
 Gerard's rubber cure ..... 68  
 German black substitute ..... 120  
     showerproofing com-  
     pounds ..... 252, 254  
 Gerner's Hevenoid ..... 126  
 Gilbert-Besaw's reclaiming proc-  
     ess ..... 296  
 Gilsonite ..... 131, 163  
 Glass, Flour of ..... 99  
     Soluble ..... 210  
 Glucose ..... 163  
 Glue ..... 163  
     Elastic ..... 161  
     Fish ..... 162  
     Waterproof ..... 139  
 Glugloss gelatine ..... 163  
 Gluten ..... 164  
 Glycerine ..... 216  
 Goa gum ..... 37  
 Godefroy's gutta-percha com-  
     pound ..... 389  
 Gold Coast rubber ..... 20  
 Gold, Oxide of ..... 100  
 Golden antimony sulphide ..... 66, 191  
 Golding's Rubberic, Formula for ..... 135  
 Goldstein's unvulcanized washers ..... 138  
 Golf balls, Gutta-percha ..... 385  
     Hard core ..... 146  
 Goodyear's, Charles, hot vulcan-  
     ization ..... 55  
     lead acetate patent ..... 101  
     triple compound ..... 114, 248  
     Nelson, india rubber  
     leather ..... 126

- Gossypium herbaceum* ..... 215  
 Gottsch, methods for analyzing vulcanized rubber. 329  
 Grahamite ..... 131  
 Grand Bassam rubber ..... 20  
 Grape rubber ..... 125  
 Graphite ..... 100  
     black ..... 179  
 Graves' Rubberite, Formula for. 135  
 Grease, French wool..... 216  
 Green, Chrome ..... 183  
     gutta-percha ..... 383  
     Hungarian ..... 183  
     pigments for rubber.... 183  
     Saxon ..... 183  
     Terra-verte ..... 183  
     Ultramarine ..... 184  
 Gregory and Thom's reclaiming process ..... 297  
 Grena Mexican rubber..... 31  
 Greytown scrap rubber..... 14  
 Griffith's white ..... 188  
 Griscom's substitute ..... 125  
 Grist's Oxolin ..... 132  
 Gront and Moore's repair cement 125  
 Guatemala rubber ..... 15  
 Guayaquil strip rubber ..... 15  
 Guayule rubber ..... 16  
 Gubbin's reclaiming process.... 297  
 Gum acacia ..... 153  
     Acroides ..... 153  
     Ammoniacum ..... 154  
     anime ..... 155  
     arabic ..... 155  
     Botany Bay ..... 153  
     British ..... 158  
     camphor ..... 158  
     carbo ..... 125  
     Carn ..... 159  
     Carrol ..... 121  
     Cherry ..... 160  
     copal ..... 160  
     dammar ..... 161  
     elemi ..... 162  
     euphorbia ..... 34  
     fibrine ..... 125  
     goa ..... 37  
     juniper ..... 165  
     Kauri ..... 165  
     lini ..... 165  
     Manila ..... 166  
     myrrh ..... 167  
     olibanum ..... 167  
     sandarac ..... 171  
     Seiba ..... 42  
     Senegal ..... 171  
     Spruce ..... 173  
     thus ..... 174  
     tragacanth ..... 174  
 Gum—*Continued*  
     tragasol ..... 174  
     Xanthorrhœa ..... 175  
 Gun cotton ..... 146  
 Gutta, Bassia ..... 37  
     Book ..... 26  
     Cotie ..... 27  
     Grek ..... 37  
     Grip ..... 38  
     Horfoot ..... 37  
     Jintawan ..... 39  
     Karite ..... 38  
     Penang ..... 27  
     Percha ..... 26, 376  
         analyses of ..393, 396, 397  
         Artificial, French .... 120  
         Bandjermassin .... 26, 378  
         cements ..... 392  
         Classification of ..... 378  
         Cleaning of ..... 380  
             Chemical ..... 382  
             Mechanical ..... 380  
         compounds ..... 387, 392  
         destruction, Causes of 386  
         Dielectric strength of. 385  
         Effect of heat on.... 376  
         Electric properties of. 385  
         extracted from leaves. 383  
         French substitute for. 125  
         golf balls ..... 385  
         Green ..... 383  
         Hard ..... 385, 386  
         Indian ..... 41  
         Liquid ..... 388  
         Macassar red ..... 26, 378  
         Properties of ..... 384  
         Reboiled ..... 379  
         resins ..... 395  
         Specific gravity of .... 383  
         Uses of ..... 384  
         Vulcanization of .... 389  
         waste ..... 293  
         Waste of ..... 381  
     Pure ..... 377  
     Shea ..... 37  
     Siak ..... 26  
     Souni ..... 27  
     Susu ..... 38  
     Yellow ..... 43  
 Guttaline ..... 125  
 Gypsum ..... 100  
 HALF Jack rubber ..... 20  
 Hall's reclaiming process ..... 293  
     process for uniting rubber to metal ..... 260  
 Hancock's gutta-percha compounds ..... 388, 391

- Hancock's—*Continued*  
vapor cure ..... 60  
*Hancornia Speciosa* ..... 16  
Hard rubber compounds ..... 371  
Manufacture of ..... 141, 371  
substitutes ..... 141  
Harmer's substitute ..... 126  
Harries' formula for rubber ..... 271  
rubber researches ..... 271  
Harris's rubber cure ..... 56  
Hatchetine ..... 166  
Havermann's rubber cure ..... 38  
Hayward's reclaiming process ..... 294  
Heat cure ..... 54  
Hebblewaite and Holt's process ..... 251  
Heckel and Schlagdenhauffen's  
analyses of gutta-  
percha ..... 396  
Heinrichsen and Marcusson on  
rubber resins ..... 308  
Heinzerling's reclaiming process,  
294, 297  
Helbronner and Bernstein's ultra  
violet rays cure ..... 61, 62  
Helenite ..... 164  
Helfer's process for coagulation ..... 49  
Helm's rubber cure ..... 58, 65  
Hematite ..... 184  
Henriques' analysis of vulcan-  
ized rubber ..... 312  
analyses of oil substi-  
tutes (table) ..... 118  
Henri's ultra violet rays cure .. 61  
Heptane ..... 237  
Hermizing process ..... 57  
*Hevea Brasiliensis* ..... 9  
latex, Analysis of ..... 44  
Plantation ..... 71  
Heve rubber ..... 39  
Heveenite ..... 126  
Heveenoid ..... 126  
Heyl-Dia's reclaiming process .. 297  
Hinrichsen's review of synthetic  
rubber ..... 270  
Honduras strip rubber ..... 15  
Honeycomb sulphur ..... 67  
Hopkinson's Vulcanine ..... 139  
Hungarian green ..... 183  
Hunter's Ossein patent ..... 106  
gutta-percha compound ..... 388  
Lanichol ..... 218  
Huth's Insulite ..... 126  
Hyaline ..... 146  
Hyatt and Penn's reclaiming  
process ..... 297  
Hydrocarbon black ..... 179  
rubber ..... 126  
Hydrochloric acid ..... 201  
Hydrogen peroxide ..... 201  
Hydrolaine ..... 126  
Hydrolene ..... 217  
Hyposulphite, Lead ..... 67  
Sodium ..... 209  
IDRIALIN ..... 164  
Idrialit ..... 164  
Ikelemba rubber ..... 23  
India rubber leather ..... 126  
Solubility of ..... 228  
Indian gutta-percha ..... 41  
hemp rubber ..... 39  
red ..... 185  
Indigo blue ..... 181  
*Indigofera* ..... 181  
Infusorial earth ..... 100  
Inrig ..... 267  
Insolacit ..... 147  
Insulate ..... 147  
Insulated wire, Compounds for ..... 369  
Manufacture of ..... 368  
Insulation, Bureau of Standards'  
methods of analy-  
sis of ..... 319  
Compounds for ..... 369  
Mavall's tape ..... 107  
Mulholland's ..... 107  
Joint Rubber Insulation  
Committee's out-  
line of analysis of  
(table) ..... 322  
Specification for 30 per  
cent. *Hevea* ..... 333  
Submarine cable ..... 387  
Insullac ..... 147  
Insulite ..... 126  
Iodide, Zinc ..... 212  
Iodine ..... 67  
*Ipomæa bona-nox* ..... 48  
Ireson's packing compound ..... 126  
Iron, Carburet of ..... 95  
oxide red ..... 185  
peroxide ..... 185  
pyrites ..... 101  
Isanga rubber ..... 23  
Isinglass ..... 164  
Islands fine Para rubber ..... 11  
Isolatine ..... 147  
Isoprene ..... 237, 271  
Rubbers from ..... 272  
Itaituba rubber ..... 11  
JACKSON'S printers' rollers com-  
pound ..... 126  
Japan wax ..... 217  
Java rubber ..... 25, 29

- Jelutong .....25, 39  
     resin ..... 164  
 Jeque rubber ..... 16  
 Jet black ..... 179  
 Jevé rubber ..... 39  
 Jintawan gutta ..... 39  
 Johnstone's non-drying compound 127  
 Joint Rubber Insulation Committee, Calculation of analyses of ..... 321  
     Methods of analysis of, ..... 321, 322  
     outlines of analysis..... 322  
     Requirements of specifications of....333, 334  
     Specifications, by whom adopted ..... 337  
 Jones' substitute ..... 127  
 Joselyn's rubber cure ..... 57  
 Jungbluth's compound ..... 127  
 Juniper gum ..... 165  
 Just's acid-proof composition... 127  
  
 KAMPTULICON ..... 127  
 Kaolin ..... 101  
 Kapak ..... 131  
 Karavodine's reclaiming process 297  
 Karite gutta ..... 38  
 Kasenoid ..... 147  
 Kassai rubber ..... 23  
 Katanga rubber ..... 23  
 Kau Drega gum ..... 41  
 Kauri gum ..... 165  
 Keene's gutta-percha compound. 391  
 Kelgum ..... 127  
 Kellogg's Kelgum ..... 127  
 Kelley's process for bronze effect  
     on rubber-coated fabrics ..... 249  
 Kempeff's hard rubber substitute 147  
 Keratite ..... 147  
 Keratol ..... 147  
 Kerite ..... 127  
     Formula for ..... 128  
 Kermes ..... 101  
 Kerosene ..... 217  
 Kessler's reclaiming process .... 297  
 Kyanizing process ..... 254  
 Kiel's compounds ..... 148  
 Kieselguhr ..... 101  
 King's yellow ..... 192  
 Kirrage compound ..... 128  
 Kittel's reclaiming process .... 297  
 Klein, Link and Gottsch's aniline  
     method for analysis of vulcanized rubber ..... 323  
 Koalatex ..... 49  
  
 Koener's reclaiming process.... 297  
 Kommoid ..... 128  
 Koneman's reclaiming process 297  
 Kornite ..... 148  
 Kremnitz white ..... 188  
 Kwilu rubber ..... 23  
  
 LA BELLE's mineral rubber..... 131  
 Laboratory, Equipment of works 303  
 Lac ..... 171  
     Button ..... 158  
     Garnet ..... 163  
     Mexican ..... 171  
     Mineral ..... 153  
 Lactitis ..... 148  
 Lagos rubber ..... 21  
 Lahou rubber ..... 19  
 Lake Leopold rubber ..... 22  
*Lallemantia iberica* ..... 218  
     oil ..... 218  
 Lamina fiber ..... 149  
 Lampblack ..... 179  
 Lamplough's Volenite ..... 138  
 Lamu ball rubber ..... 24  
*Landolphia* ..... 7  
     *Carpodinus* ..... 9  
     *Clitandras* ..... 9  
 Lang's Novelty rubber ..... 131  
 Lanichol ..... 218  
 Lanolate, Aluminum ..... 213  
 Lanolin ..... 218  
 Lard oil ..... 219  
*Larix Europea* ..... 245  
 Lascelles-Scott on naphtha .... 240  
     methane rubber solvents 239  
     on mineral wool ..... 105  
 Latex, Rubber ..... 8  
     Adulteration of rubber.. 34  
         Amapa ..... 34  
         Molango ..... 34  
         Sucuba ..... 34  
         Surva ..... 34  
         Tamanguiro ..... 34  
     Analysis of *Hevea*.. 44, 266  
 Lavender oil ..... 219  
*Lavandula vera* ..... 219  
 Lead acetate ..... 101, 202  
     Blue ..... 93  
         carbonate ..... 101  
         nitrate ..... 202  
         oxide ..... 102  
         oxychloride ..... 102  
         peroxide ..... 102  
         Red ..... 110  
         Sublimed ..... 112  
         Sugar of ..... 102, 112, 202  
         sulphate ..... 102



- Lead—*Continued.*  
  sulphide ..... 68, 180  
  White ..... 113  
Leadbetter's Metalined rubber..... 130  
Leather, Cooley's artificial..... 102  
Leatherine ..... 128  
Leatheroid ..... 149  
Leathrubber compound ..... 128  
Lemon oil ..... 219  
Leonard's substitute ..... 128  
Lessnenn and Weinkopf's formula ..... 251  
Leva's drying process ..... 46  
Liberian rubber ..... 20  
Liconite ..... 128  
Ligroin ..... 240  
Lime ..... 49, 102  
  juice ..... 49  
  Phosphate of ..... 94  
Limeite ..... 129  
Lini gum ..... 165  
Linoxin ..... 129  
Linseed oil ..... 220  
  Manganated ..... 221  
*Linum usitatissimum* ..... 220  
Liquid rubber ..... 131  
Liquor of flint ..... 202  
Litharge ..... 103  
Lithargrite ..... 103  
Lithographic varnish ..... 220  
Lithopone (lithophone) ..... 104, 188  
Lithro-carbon ..... 165  
Little known rubbers ..... 32  
Liver of sulphur ..... 67  
Liverpool pressed rubber ..... 18  
Loanda rubber ..... 23  
Loango rubber ..... 21, 23  
Lombiro rubber ..... 24  
Lomi ball rubber ..... 21  
Lopori rubber ..... 22  
Loranthus rubber ..... 39  
Lucas's gutta-percha compound. 391  
Luff, B. D. W., on synthetic rubber ..... 269  
Luff's celluloid rubber ..... 129  
Lugo ..... 129  
  rubber ..... 129  
Lump rubber, African ..... 18  
Luvituku rubber ..... 22
- Machines—*Continued.*  
  Van den Kerckhove's fumero ..... 51  
  Wickham's ..... 51  
Macintosh's gutta-percha compound ..... 388  
Mackintoshes, Manufacture of.. 364  
MacMahon's Maponite ..... 129  
Macwarrieballi gum ..... 39  
Madagascar rubber ..... 24  
  Black ..... 24  
  Pinky ..... 24  
Madanite ..... 129  
Madeira rubber ..... 12  
Magnesia, Heavy calcined ..... 104  
  Light calcined ..... 104  
Maize oil ..... 215  
Majunga rubber ..... 24  
  Brown cure ..... 24  
  niggers ..... 24  
  Unripe ..... 24  
Malaya rubber ..... 29  
Male rubber ..... 42  
Mana ..... 38  
Manaos rubber ..... 12  
Mandarnva rubber ..... 39  
Mangegatu gum ..... 39  
Mangabeira rubber ..... 16  
Manga-ice rubber ..... 39  
Manganated linseed oil ..... 221  
Manganese, Destruction of rubber by ..... 105  
  Peroxide ..... 104  
*Manihot dichotoma* ..... 16  
  *Glaziovii* ..... 16  
Manila gum ..... 166  
Manjak ..... 166  
Manoh twist rubber ..... 20  
Manufacture of rubber goods... 351  
Maponite ..... 129  
Marble flour ..... 105  
Marcy's rubber cure ..... 55, 56, 57  
Marks' reclaiming process ... 294, 298  
Marloid ..... 149  
Massaranduba rubber ..... 39  
Massicot ..... 105  
Mastic ..... 166  
Matthew's process for colored designs on proofed fabrics ..... 249  
Matto Grosso rubber ..... 13  
Mayall's reclaiming process... 295  
  tape insulation ..... 108  
Mayumba rubber ..... 21  
Mechanical rubber goods, Analysis of ..... 315  
  Compounds for ..... 355  
  Manufacture of ..... 354
- McCARTNEY's reclaiming process 295  
Maboa gum ..... 39  
Machacon juice ..... 49  
Machines, Coagulating ..... 50  
  Beta separator ..... 50  
  Coutinho's ..... 50  
  DaCosta's ..... 51  
  Danin's ..... 50



- Medium Para rubber ..... 11  
 Menthol ..... 166  
 Metalined rubber ..... 130  
 Metals, Attaching rubber to... 259  
     on rubber, Action of... 262  
 Methane rubber solvent ..... 239  
 Mexican lac ..... 171  
     plantation rubber ..... 31  
     rubber ..... 15  
 Meyer's rubber cure ..... 58  
 Mica ..... 105  
 Micanite ..... 149  
 Milk of sulphur ..... 68  
 Milling rubber ..... 353  
 Mimo-tannic acid ..... 202  
*Mimusops balata* ..... 398  
 Mineral india rubber asphalt ... 166  
     lac ..... 153  
     oil, Russian ..... 225  
     rubber ..... 130  
     tallow ..... 166  
     wax ..... 167  
     wool ..... 105  
 Minium ..... 106  
 Mirbane oil ..... 221  
 Miscellaneous processes ..... 247  
 Mitchell's reclaiming process... 294  
 Mixing rubber ..... 353  
 Molded rubber goods, Compounds 370  
     Manufacture of ..... 369  
 Mollendo rubber ..... 13  
 Molybdenum blue..... 181  
 Mongalla rubber ..... 22  
 Montpellier, Analysis of gutta-  
     percha by ..... 393  
 Morat white ..... 188  
 Morgan's Ce-re-gum ..... 144  
 Moroccoline ..... 131  
 Morondava rubber ..... 24  
 Mosley's process for ornament-  
     ing proofed fabrics 251  
 Mossamedes rubber ..... 23  
 Mt. Prospect Laboratory methods  
     of analysis of vul-  
     canized rubber ... 329  
 Moudan white ..... 188  
 Mountain flour ..... 106  
     milk ..... 99  
 Mowbray, Preservation of rub-  
     ber goods by .... 258  
 Mozambique rubber ..... 23  
 Mudar gum ..... 39  
 Mule gum ..... 43  
 Mulholland's insulation com-  
     pound ..... 107  
 Mullee's rubber cure ..... 59  
 Muriate of ammonia ..... 202  
 Muriatic acid ..... 202  
 Murphy's rubber cure ..... 58  
     reclaiming process .... 298  
*Musa paradisiaca* ..... 34  
     *sapientum* ..... 34  
 Musa Gum ..... 40  
 Mustard oil ..... 221  
 Myrrh ..... 167  
 NAGEL's patent Con-current rub-  
     ber ..... 122  
 Namaqualand rubber ..... 40  
 Nantusi ..... 68  
 Naphtha ..... 239  
     Boiling points of ..... 241  
     Bone ..... 237  
     Coal-tar ..... 240  
     Pentane ..... 241  
     Petroleum ..... 240  
         Benzine ..... 240  
         Gasoline ..... 240  
         Ligroin ..... 240  
         Rhigolene ..... 240  
     specific gravity of  
         (table) ..... 241  
 Naphthalene ..... 239  
 National Board of Fire Under-  
     writers' Labora-  
     tories' methods of  
     analysis ..... 321  
 Natural pitch ..... 167  
 Nature of india rubber ..... 7  
 Neatsfoot oil ..... 221  
 Neen rubber ..... 40  
 Negroheads ..... 11  
 Neilson's reclaiming process... 298  
 New Caledonia rubber ..... 27  
 Newbrough's and Fagan's rubber  
     cure ..... 64  
 Newbrough's rubber cure ..... 57  
 Newmastic ..... 267  
 Nicaragua rubber ..... 14  
 Nickels' rubber cure ..... 60  
 Niger rubber ..... 21  
 Nigeria rubbers ..... 21  
 Niggers, African rubber ..... 19  
     Sierra Leone ..... 20  
 Nigrite ..... 149  
 Nigrum Elasticum ..... 131  
*Nipa fruticans* ..... 49  
     salt ..... 49  
 Nitrate, Lead ..... 202  
 Nitric acid ..... 202  
 Nitrobenzene ..... 221  
 Nitrobenzol ..... 221  
 Nitrocellulose ..... 149  
 Notion rubber trade, Compounds  
     for ..... 374  
     manufacture ..... 374

- Novelty rubber substitute ..... 131  
 Nut-gall ..... 203  
 Nuts, African rubber ..... 18
- OBACH, Analysis of gutta-percha  
     by ..... 397  
     composition of gutta-  
     percha resins ..... 397
- Ocotillo rubber ..... 40  
 Oceanica rubber ..... 27  
 Ocher, Red ..... 185  
     Yellow ..... 193  
 Ohmlac ..... 132  
 Oil, Blown ..... 213  
     Camphor ..... 214  
     Caoutchouc ..... 214  
     Castor ..... 214  
     Cod-liver ..... 214  
     Colza ..... 215, 224  
     Consolidated ..... 215  
     Corn ..... 215  
     Cottonseed ..... 215  
     Creosote ..... 215  
     Derry's waterproof har-  
     ness ..... 226  
     Dippel's ..... 237  
     Eucalyptus ..... 215  
     Fish ..... 216  
     Fusel ..... 231  
     Kerosene ..... 217  
     Lallemantia ..... 218  
     Lard ..... 219  
     Lavender ..... 219  
     Lemon ..... 219  
     Linseed ..... 219  
     Maize ..... 215  
     Manganated linseed .. 221  
     Mirbane ..... 221  
     Mustard ..... 221  
     Neatsfoot ..... 221  
     of vitriol ..... 203  
     Olive ..... 222  
     Origanum ..... 226  
     Orris ..... 222  
     Palm ..... 222  
         Congo ..... 223  
         Lagos ..... 223  
         White ..... 223  
     Peppermint ..... 223  
     Petroleum ..... 224  
     Pine ..... 244  
     Poppyseed ..... 225  
     Rapeseed ..... 215, 225  
     Rock ..... 224  
     Rosemary ..... 225  
     Rosin ..... 225, 244  
     Russian mineral ..... 225
- Oil—*Continued*  
     Shale ..... 225  
     Tar ..... 226  
     Thyme ..... 226  
     Turpentine ..... 226, 245  
     Vulcanized ..... 227  
     Walnut ..... 227  
     White drying ..... 227  
         Rangoon ..... 224  
         Wormwood ..... 227  
     Oils used in rubber compounds. 213  
     Okonite ..... 132  
     Old Calabar rubber ..... 20, 21  
     Oleargum ..... 222  
     Oleic acid ..... 203  
     Oleo resins ..... 167  
     Oleum white ..... 188  
     Olibanum gum ..... 167  
     Olive oil ..... 221  
     Olivier's ultra violet rays cure.. 61  
     Olsson's Zackingummi ..... 140  
     Optimum cure ..... 71, 345  
     Orange ball rubber ..... 23  
         mineral ..... 106  
         vermillion ..... 185  
     Orinoco rubber ..... 13  
     Orris oil ..... 222  
     Orr's white ..... 189  
     Ossein ..... 106  
     Ostromislensky's theory of vul-  
         canization ..... 275  
     Oxalic acid ..... 203  
     Oxidation and vulcanization, Ve-  
         locity of ..... 285  
     Oximony ..... 185  
     Oxolin ..... 132  
     Oxydases in crude rubber ..... 52  
     Oysters, African ..... 19  
     Ozocerine ..... 167  
     Ozocerite ..... 168
- PAGODITE ..... 106  
 Pala gum ..... 40  
 Palm oil ..... 222  
     Congo ..... 223  
     Lagos ..... 223  
     White ..... 223  
 Palo Amarillo gum ..... 41  
     colorado ..... 41  
 Panama rubber ..... 15  
 Pantasote ..... 149  
*Papaver somniferum* ..... 225  
 Para rubber ..... 10  
 Paraffin wax ..... 168, 223  
 Paragol ..... 132  
 Paris black ..... 180  
     white ..... 107  
 Parkesine ..... 132

- Parkes's gutta-percha compound 391  
 surface colors ..... 247  
 Parmelee's rubber cure ..... 57  
*Parthenium argentatum* ..... 17  
 Passmore's reclaiming process.. 298  
 Paste rubbers, African ..... 18  
 Pau rubber ..... 39  
*Payena* ..... 43  
 Payen's analysis of gutta-percha 397  
 lead acetate patent .... 101  
 Pectous rubber ..... 308  
 Pedryoid ..... 133  
 Pegamoid ..... 149  
 Penang rubber ..... 25  
 Pensa's rubber ..... 133  
 Pentane ..... 241  
 Pentasulphide, Antimony ..... 68  
 Penther's reclaiming process ... 298  
 Peppermint oil ..... 223  
 Perchoid ..... 133  
 Permanent white ..... 93, 107  
 Pernambuco rubber ..... 16  
 Peroxide, Iron ..... 185  
 Hydrogen ..... 202  
 substitutes ..... 133  
 Peruvian rubber ..... 13  
 Peterson's reclaiming process... 298  
 Petrifite ..... 106  
 Petrolatum ..... 223  
 Petroleum jelly ..... 224  
 naphtha ..... 240  
 oil ..... 224  
 Rangoon white ..... 224  
 solvents ..... 241  
 Phenol ..... 204  
 Phosphate of sodium ..... 209  
 Phosphorus ..... 106  
 Physical testing of rubber goods,  
 302, 337  
 Air brake and signal hose 343  
 Bursting tests of .... 345  
 Friction test of..... 344  
 Porosity test of..... 344  
 Stretching test of cover  
 and tube of..... 344  
 Tensile strength of  
 tube and cover of 344  
 Test specimen of .... 343  
 Defects of test pieces for 343  
 Set in ..... 342  
 Bar test pieces for ... 343  
 Ring test pieces for... 343  
 Standard methods of.... 338  
 Temperature ..... 339  
 Tensile strength ..... 339  
 Time ..... 339  
 Tensile strength deter-  
 mination ..... 341  
 across the seam ..... 342  
 Physical testing of rubber  
 goods—*Continued*.  
 Tensile strength—*Continued*.  
 Apparatus for ..... 341  
 bar test pieces for,  
 Marking ..... 341  
 Measurement of .... 341  
 Breaking ..... 341  
 breaking point, Elongation at..... 342  
 Grips ..... 341  
 ring test pieces.. 341, 342  
 ring test pieces, Measurements of ..... 341  
 test pieces, Preparation of 339  
 Averages ..... 338  
 Elongation ..... 339  
 Friction ..... 340  
 Sampling ..... 338  
 Set ..... 339  
 Pickeum gum ..... 41  
 substitute ..... 133  
*Picradenia floribunda utilis* ... 41  
 Pigments for coloring rubber... 176  
 Pine oil ..... 244  
*Pinus maritima* ..... 175  
*palustris* ..... 175  
*Sylvestris* ..... 244  
 Pioneer mineral rubber ..... 131  
 Pipe clay ..... 107  
*Pistacia lentiscus* ..... 175  
 Pitch ..... 169  
 Black ..... 158  
 Burgundy ..... 158  
 Coalite ..... 160  
 Jews ..... 155  
 Natural ..... 167  
 Stearine ..... 173  
 Vegetable ..... 175  
*Pithecolobium bigeminum* ..... 207  
 Plantation rubber ..... 27  
 Forms of ..... 31  
 Biscuits ..... 29  
 Block ..... 30  
 Crêpe ..... 29  
 Flake ..... 30  
 Lace ..... 30  
 Scrap ..... 30  
 Sheets ..... 29  
 Worm ..... 30  
*Hevea*, Optimum cure of 71  
 Market names of..... 30  
 Amber crêpe ..... 30  
 Brown crêpe ..... 30  
 Ceara ..... 31  
 Central American .... 31  
 Ceylon *Castilloa* .... 31  
 Colombo scrap ..... 31

- Plantation rubber—*Continued*.  
 Market names of—*Con*.  
   Congo ..... 31  
   First latex crêpe..... 30  
   Guayaquil *Castilloa* .. 31  
   Java *Castilloa* ..... 31  
   Mexican ..... 31  
   Rambong ..... 31  
   Smoked Sheet, plain  
     standard quality.. 31  
     ribbed standard  
       quality ..... 31  
   Tobago ..... 31  
   Trinidad ..... 31  
   Uganda ..... 31  
   Unsmoked Sheet,  
     standard quality.. 31  
   West Indies ..... 31  
 World's Annual produc-  
   tion of (table).... 28  
 Plaster of Paris ..... 107  
 Plasters, Compounds for..... 375  
   Manufacture of..... 375  
 Plasticon ..... 150  
 Plastite ..... 150  
 Plumbagine ..... 108  
 Plumbago ..... 108  
 Ponolith ..... 189  
 Pontianak rubber ..... 26  
   Pressed ..... 26  
   Refined ..... 26  
 Poppenhusen reclaiming process. 295  
 Poppyseed oil ..... 225  
 Portland cement ..... 108  
 Potash ..... 204  
   caustic ..... 205  
 Potassium acid tartrate ..... 204  
   arsenate ..... 204  
   bichromate ..... 204  
   bisulphate ..... 204  
   carbonate ..... 204  
   cyanide ..... 205  
   hydroxide ..... 205  
   permanganate ..... 205  
 Potato celluloid ..... 150  
 Pouckpong gum ..... 42  
 Powdered coal ..... 109  
 Pozelina ..... 49  
 Pratt Vulcaneston ..... 152  
 Preserving rubber goods, Proc-  
   esses for ..... 257  
   Benton's ..... 258  
   Elworthy's ..... 258  
   Kreusler and Bude's .... 257  
   Mowbray's ..... 258  
   Trueman's ..... 258  
   Truss' ..... 259  
   under water ..... 257  
   Zingler's ..... 259  
 Presspahn ..... 150  
 Pressure cure ..... 62  
 Price (American) reclaiming  
   process ..... 298  
   (English) reclaiming  
     process ..... 298  
 Prince's metallic paint ..... 185  
 Printing on inflatable rubber  
   films ..... 248  
 Proofed fabrics, Compounds for. 364  
   Manufacture of ..... 364  
   Ornamenting ..... 248  
 Properties in rubber, Relation-  
   ship of mechanical  
     to chemical..... 345  
   Depolymerization ..... 346  
   Optimum cure ..... 345  
   Stress-strain type curve. 348  
 Propylene chloride ..... 244  
 Proto-chloride, Sulphur ..... 68  
 Prussian blue ..... 181  
   red ..... 185  
 Pumice ..... 109  
 Puncture fluids and tire fillers.. 266  
   Campbell and Cushman's 266  
   Cellazote ..... 267  
   Cyclo ..... 266  
   Dow's ..... 266  
   Elastes ..... 266  
   Everlastic ..... 266  
   Fagioli's ..... 266  
   Frankenburg's ..... 266  
   Inrig ..... 267  
   Newmastic ..... 267  
   Puncture Closer ..... 267  
   Roland's ..... 267  
   Rubber foam ..... 267  
   Rubberine ..... 268  
   Scott's ..... 268  
   Suber's ..... 268  
   Tire Life ..... 268  
 Purcellite ..... 133  
 Purub ..... 49  
 Purus rubber ..... 12  
 Puzzolana ..... 110  
 Pyroxylin ..... 150  
 P. F. U. gum..... 41  
*QUERCUS infectonia* ..... 203  
 Quicklime ..... 205  
 Quinn's rubber ..... 134  
 Quittah niggers rubber ..... 20  
 RAMBONG plantation rubber .... 31  
 Rangoon rubber ..... 25  
 Rapeseed oil ..... 215, 225  
 Rate of cure of plantation Para  
   rubber ..... 73, 311



- Rate of cure of plantation Para rubber,—*Continued.*  
 Eaton and Grantham on causes of variability in .....71, 73  
 Analytical work of.... 75  
 Conclusions of ....74, 75  
 Experiments of ....73, 75  
 Nitrogen content and 75  
 Summary on ..... 77  
 Schidrowitz on ..... 72  
 Rathite ..... 134  
 Raven mineral rubber ..... 131  
 Raymond's rubber cure ..... 61  
 Reagents for rubber analysis ... 315  
 Reclaimed rubber ..... 290  
     U. S. annual production of ..... 290  
 Reclaiming rubber, Processes for 292  
     Alexander's ..... 295  
     Anderson's ..... 295  
     Baschnagel's ..... 293  
     Basle's ..... 296  
     Beylikgy's ..... 295  
     Bourn's ..... 294  
     Brimmer's ..... 296  
     Chautard's ..... 296  
     Chemical ..... 291  
     Clapp's ..... 293  
     Clift's ..... 296  
     Durvez's ..... 296  
     Eves's ..... 296  
     Faure's ..... 294  
     French ..... 296  
     Gilbert-Besaw's ..... 296  
     Gregory and Thom's ... 297  
     Gubbin's ..... 297  
     Hall's ..... 293  
     Hayward's ..... 294  
     Heinzerling's ..... 294, 297  
     Heyl-Dia's ..... 297  
     Hyatt and Penn's ..... 297  
     Karavodine's ..... 297  
     Kessler's ..... 297  
     Kittel's ..... 297  
     Koener's ..... 297  
     Koneman's ..... 297  
     McCartney's ..... 295  
     Machinery used for .... 292  
     Marks' ..... 294, 298  
     Mayall's ..... 295  
     Mechanical ..... 291  
     Mitchell's ..... 294  
     Murphy's ..... 298  
     Neilson's ..... 298  
     Passmore's ..... 298  
     Penther's ..... 298  
     Peterson's ..... 298  
     Poppenhusen's ..... 295  
 Reclaiming rubber—*Continued.*  
     Price's (American) .... 298  
     (English) ..... 298  
     Roux's ..... 298  
     salt ..... 206  
     Simond's ..... 295  
     Spence's ..... 299  
     Steenstrup's ..... 298  
     Theilgaard's ..... 298  
     Torstrick's ..... 294  
     Wheeler's ..... 298  
     Zuhl's ..... 299  
 Red Antimony sulphide ..... 66  
     Antimony crimson sulphide ..... 184  
     chalk ..... 109  
     hematite ..... 185  
     Indian ..... 185  
     Iron oxide ..... 185  
     Peroxide ..... 185  
     lead ..... 110  
     ocher ..... 185  
     orange vermilion ..... 185  
     pigments for rubber ... 184  
     Prince's metallic ..... 185  
     Prussian ..... 185  
     Venetian ..... 185  
 Reid's Velvrl ..... 138  
 Remanso rubber ..... 16  
 Rennet ..... 206  
 Repin's tong oil substitute ..... 137  
 Resin, Amber  
     Jelutong ..... 164  
     Sludge oil ..... 172  
     Turpentine ..... 175  
 Resinolines ..... 134  
 Resins ..... 153, 170  
     Oleo ..... 167  
     Rubber ..... 229, 308  
 Retinasphalt ..... 170  
 Retinite ..... 170  
 Rhea gum ..... 134  
 Rhigolene ..... 240, 241, 244  
 Rice rubber ..... 134  
 Rider's gutta-percha compound.. 391  
     rubber cure ..... 58  
 Riviere's Elasteine ..... 123  
 Rock oil ..... 224  
 Roland's puncture compound... 267  
 Rosaline ..... 134  
 Rosemary oil ..... 225  
 Rosenstein's method for total sulphur in vulcanized rubber ..... 331  
 Rosin ..... 170  
     oil ..... 225, 244  
 Ross's white ..... 189  
 Rostaing's gutta-percha compound ..... 391



- Rotten stone ..... 110  
 Rouen white ..... 189  
 Roux reclaiming process ..... 298  
 Rubber, Action of metals on... 262  
     Adhesive principle of  
         crude ..... 8  
         asphalt ..... 135  
         Calendering ..... 353  
         cements ..... 372  
         Chemical formula of..8, 271  
         Coefficient of vulcaniza-  
             tion and the state  
             of cure of..... 347  
         colors, Requirements for 249  
         Deodorization of ...116, 256  
         Electroplating on ..... 248  
         Embossing of ..... 248  
         flux ..... 135  
         foam ..... 267  
         goods, Physical testing of 337  
         grades, Crude ..... 10  
         Harries formula for .... 271  
         Impregnating ..... 251  
         Insoluble matter in .... 309  
         latex ..... 8  
             Adulteration of..... 34  
             Analysis of *Hevea*, 44, 266  
         makers' white ..... 189  
         manufacture ..... 354  
             Divisions in ..... 354  
                 Boots and shoes.... 357  
                 Cement ..... 372  
                 Dental and stamp  
                     gum ..... 373  
                 Druggists', station-  
                     ers' and surgical  
                     sundries ..... 361  
                 Hard rubber ..... 371  
                 Insulated wire ..... 368  
                 Mackintoshes, proof-  
                     ing and carriage  
                     cloth ..... 364  
                 Mechanical goods .. 354  
                 Mold work ..... 369  
                 Notions ..... 374  
                 Plasters ..... 375  
                 Tires ..... 366  
             Primary processes in. 351  
                 Calendering ..... 353  
                 Drying ..... 352  
                 Milling ..... 353  
                 Spreading ..... 354  
                 Washing ..... 351  
             "Nervy" principle in..8, 308  
         Nitrogenous substances  
             in ..... 309  
         Oil substitutes for ..... 117  
             Analyses of .(table).. 118  
         Optimum cure of..... 346
- Rubber—*Continued.*  
     Physical properties of.. 7  
     pigments ..... 176  
     Preserving goods ..... 257  
     scrap ..... 292  
     Shrinkage of ..... 263  
     Solubility of (tables),  
         228, 229  
         resins (tables) ..... 229  
     solvents ..... 230  
     Sources of ..... 7  
     Specific gravity of..265, 349  
     Synthetic .....269, 274  
     tree, Male ..... 42  
     "Type" curve of crude.. 348  
     Uniting metals to..... 259  
     Valuation of crude ..... 303  
     velvet ..... 135  
 Rubberaid ..... 135  
 Rubberic ..... 135  
 Rubberine ..... 268  
 Rubberite ..... 135  
 Ruberine ..... 135  
 Ruberoid ..... 135  
 Rub-hide ..... 136  
 Russian mineral oil ..... 225
- SAL ammoniac ..... 206  
     soda ..... 206  
 Saleratus ..... 206  
 Salicylic acid ..... 206  
 Salol, vulcanized rubber solvent. 329  
 Salt .....49, 206  
     Reclaiming ..... 206  
 Saltpeter ..... 206  
 Salt-pond rubber ..... 20  
 Sandarac gum ..... 171  
 Sankuru ..... 22  
 Santos rubber ..... 16  
*Sapium biglandulosum* ..... 42  
     *tolimense* ..... 15  
*Sapotaceæ* ..... 377  
 Sarawak ..... 26  
 Sarco ..... 136  
 Sarua rubber ..... 41  
 Satin gloss black ..... 180  
 Saxon blue ..... 181  
 Schidrowitz, examination of crude  
     rubber ..... 307  
     and Goldsborough on co-  
         efficient of vulcan-  
         ization and state  
         of cure ..... 348  
         stress strain type curves 348  
 Scott's puncture fluid ..... 268  
 Seedlac ..... 171  
 Seiba gum .....41, 42

- Selenium ..... 110  
 Senegal gum ..... 171  
 Seringuina ..... 49  
 Sernamby Para rubber ..... 10, 11  
 Shale, Argillaceous red ..... 90  
     oil ..... 225  
     spirit ..... 244  
 Sharpe, Analysis of gutta-percha  
     by ..... 397  
     Composition of gutta-  
         percha by ..... 397  
 Shea butter ..... 38  
 Shellac ..... 171  
 Shepard's gutta-percha compound ..... 390  
 Showerproofing ..... 251  
     American ..... 252, 253  
     Cohuru's ..... 255  
     Cravenette ..... 251  
     English ..... 253  
     Forster's ..... 254  
     Frankenburg's ..... 255  
     German ..... 252, 254  
     Kyanized ..... 254  
     Smith's porous fabric... 255  
 Shrinkage of crude rubber  
     (tables) ..... 263, 264  
 Sierra Leone rubbers ..... 20  
 Silex ..... 110  
 Silica ..... 110  
 Silicate, Carbon black ..... 180  
     Cotton ..... 110  
 Silicon fluoride ..... 206  
 Silky Assinee rubber ..... 20  
 Siluminite ..... 150  
 Simond's reclaiming process... 295  
 Simpson's rubber cure ..... 57  
*Sinapis alba* ..... 221  
     *nigra* ..... 221  
 Size ..... 172  
 Slag wool ..... 110  
 Slaked lime ..... 110  
 Slate ..... 110  
 Sludge oil resins ..... 172  
 Smalts ..... 182  
     Analysis of (table)..... 182  
 Smith's, Thos., Theskelon cement  
     porous fabric shower-  
         proofing ..... 255  
     Willoughby, gutta-per-  
         cha compound..... 152, 387  
 Soap ..... 50, 206  
     bark ..... 207  
     Castile ..... 207  
     Resin ..... 207  
     substitutes ..... 136  
 Soapstone ..... 111  
 Soda ..... 207  
     Caustic ..... 209  
     Sal ..... 206  
 Sodium baborate ..... 207  
     bisulphite ..... 208  
     carbonate ..... 208  
     chloride ..... 208  
     hydroxide ..... 209  
     hyposulphite ..... 209  
     phosphate ..... 209  
     silicate ..... 210  
     sulphate ..... 210  
     tungstate ..... 210  
 Solicum ..... 136  
 Solubility of rubber (tables)..... 228, 229  
     of rubber resins (table). 229  
 Soluble glass ..... 210  
 Solvent, Chute's rubber resin... 236  
     Gottsch's vulcanized rub-  
         ber ..... 329  
     Twiss' vulcanized rub-  
         ber ..... 328  
 Solvents ..... 228  
     Methane ..... 239  
     Petroleum ..... 241  
     Rubber ..... 230  
     Vulcanized rubber ..... 328  
 Sorel's compound ..... 103, 151  
 Soudan rubber ..... 19  
 Spanish white ..... 189  
 "Special" brand zinc oxide ..... 190  
 Specific gravity, Determination of  
     in rubber compounding... 349  
     of rubber ..... 265  
     of petroleum n a p h t h a  
         (table) ..... 241  
 Specification, Thirty per cent.  
     *Hevea* insulation  
         compound ..... 333  
 Spence, color in crude rubber .. 52  
     "On the Relationship of  
         Mechanical to  
         Chemical Proper-  
         ties" ..... 345  
     oxydases in crude rub-  
         ber ..... 52  
     reclaiming process ..... 299  
 Spermaceti ..... 173  
 Spill's gutta-percha compound.. 389  
 Spindle rubber ..... 23  
 Spirits of turpentine ..... 245  
     of wine ..... 50  
     Wood ..... 246  
 Spreading rubber ..... 354  
 Spruce gum ..... 173  
 St. George turpentine rubber .... 138  
 Stabiliz ..... 151  
 Starch ..... 111  
 Stearine, ..... 173, 226  
     pitch ..... 173  
 Steenstrup's reclaiming process. 298

- Stevens, coefficient of vulcanization ..... 347  
     rate of cure ..... 79  
 Stick rubber ..... 23  
 Sticklac ..... 171, 173  
 Stockholm tar ..... 173  
 Storax, Balsam of ..... 156  
 Straits rubber ..... 29  
 Strasburg turpentine ..... 158  
 Suber's filler ..... 268  
 Sublimed lead ..... 111  
 Submarine cables, Insulation of ..... 387  
 Substitute, Blandy's ..... 120  
     Brown's hard rubber ..... 143  
     Carbon bisulphide ..... 234  
     Dankwerth's ..... 122  
     De Pont's ..... 145  
     Fayolles' ..... 124  
     Franklin ..... 125  
     German black ..... 120  
     Griscom's ..... 125  
     Harmer's ..... 126  
     Jones's ..... 127  
     Moroccoline ..... 131  
     Nature and use of ..... 117  
     Nigrum Elasticum ..... 131  
     Novelty rubber ..... 131  
     Ohmlac ..... 132  
     Paragol ..... 132  
     Pedryoid ..... 133  
     Perchoid ..... 133  
     Peroxide ..... 133  
     Pickeum ..... 133  
     Purcellite ..... 133  
     Resinolines ..... 134  
     Russian ..... 136  
     Soap ..... 136  
     Tong oil ..... 137  
     Wichmann's ..... 139  
     Wolfert's ..... 139  
 Sugar of lead ..... 112, 202  
 Sulo ..... 136  
 Sulphate, Sodium ..... 210  
 Sulphide, Lead ..... 68  
     Zinc ..... 68  
 Sulphur ..... 69  
     Balsam of ..... 69, 156  
     bath cure ..... 63  
     chloride ..... 65  
     fumes ..... 50  
     Honeycomb ..... 67  
     Liver of ..... 68  
     lotum ..... 69  
     Milk of ..... 68  
 Sulphuret, Antimony ..... 66  
 Sulphuric acid ..... 210  
 Sumatra rubber ..... 29  
 Surface colors ..... 247  
     printing ..... 247  
 Susu-poko gum ..... 41  
 Synthetic rubber ..... 269  
     Available sources of ..... 273  
     Butanes ..... 272  
     Early investigations on ..... 269  
     dimethyl butanes ..... 272  
     History of ..... 269, 270  
     Isoprene ..... 271, 272  
     Practical utility of ..... 273  
     Production of ..... 270  
 TABBYITE ..... 136  
*Tabernaemontana Thurstoni* ..... 41  
 Talaing rubber ..... 41  
 Talc ..... 111  
 Talite ..... 112  
 Tallow ..... 226  
     Mineral ..... 166  
 Talotalo gum ..... 41  
 Tamatave rubber ..... 24  
     Pinky ..... 24  
 Tannic acid ..... 211  
 Tannin ..... 211  
 Tar ..... 174  
     Birch bark ..... 157  
     Candle ..... 159  
     oil ..... 226  
     Stockholm ..... 173  
 Tarpaulin compound ..... 102  
 Tartaric acid ..... 211  
 Tava rubber ..... 23  
 Taylor's Purcellite ..... 133  
 Terra-verte ..... 183  
     Analysis of ..... 184  
 Tetrachloride, Carbon ..... 235, 244  
 Tetrachlormethene benzene substitute ..... 244  
 Texoderm ..... 151  
 Textiloid ..... 137  
 Theilgaard's reclaiming process ..... 298  
 Thenard's blue ..... 182  
 Theskelon cement ..... 137  
 Thimbles, African ..... 18  
 Thion ..... 245  
 Thomas's rubber cure ..... 56  
 Thus, Gum ..... 174  
 Thyme oil ..... 226  
*Thymus vulgaris* ..... 226  
 Tin oxide ..... 113  
 Tire Life ..... 268  
 Tires, Compound for ..... 367  
     Manufacture of ..... 366  
 Tirucalli gum ..... 42  
 Tobago plantation rubber ..... 31  
 Togoland rubber ..... 21  
 Tolu balsam ..... 174  
 Toluene ..... 245

Toluol .....	245	Uniting rubber to metals, Proc-	
Tong oil substitutes .....	137	esses for— <i>Continued.</i>	
Tongues, African .....	19	Garrrity and Avery's....	260
Toonu gum .....	42	Hall's .....	260
Torres' system of coagulation...	50	melting .....	259
Torstrick's reclaiming process..	294	solid tires .....	260
Touchpong gum .....	42	Upper Congo rubber .....	22
Tragacanth, Gum .....	174	Upriver rubber .....	12
Tragasol, Gum .....	174	Uranium sulphide .....	180
Tremenol .....	137		
Trinidad asphalt .....	174	VAPOR cure .....	54
plantation rubber .....	31	Variability in rate of cure,	
Triple compound, Goodyear's...	113	Causes of .....	71
Tripoli .....	112	Varnish, Boot and shoe .....	361
Trotter's rubber cure .....	55	Lithographic .....	220
Troye's white .....	189	Vaseline .....	226
Trueman, preservation of rubber		Vegetable pitch .....	175
goods .....	258	Vegetaline .....	151
Truss, preservation of rubber		Velvrl .....	138
goods .....	259	Venetian red .....	185
Tu Chung rubber .....	42	Vermilion .....	186
Tungstate, Sodium .....	210	Vesuvian white .....	70
Tungstic acid .....	212	Virgin rubber .....	15
Tuno gum .....	42	Viscoid .....	151
Tunu gum .....	43	Viscose .....	151
Turnbull's rubber paint.....	137	Viscosity of crude rubber.....	311
Turner's yellow .....	102	Vitriol, Oil of .....	203
Turpentine .....	175, 226	Vitrite .....	151
Bordeaux .....	175	Volenite .....	138
China .....	175	Voltax .....	138
Crude .....	245	Voltit .....	138
Oil of .....	226, 245	Vorite .....	139
resin .....	175	Vulcabeston .....	152
rubber .....	138	Vulcanina .....	139
Spirits of .....	245	Vulcanine .....	70, 139
Strasburg .....	158	Vulcanization, Coefficient of...	311
Venice .....	175	Gutta-percha .....	389
Turpin's hydrocarbon rubber ...	126	Ostromislensky's theory	
Tuxpam strip rubber .....	15	of .....	281
Twiss' solvent for vulcanized		process of, Ayling's ....	58
rubber .....	328	Banigan's .....	57
Twist, African .....	19	Bernstein's .....	61, 62
Sierra Leone .....	20	Caulbry's .....	60
Tyer's white rubber .....	189	Cold .....	54, 59
Types of Plantation Para .....	30	Dieffenbach's .....	56
Tyre-lith .....	112	Eaton's, A. K. ....	56
		Electric .....	63
		Elmer's .....	59
UGANDA rubber .....	23	Falke and Richards'..	56
plantation .....	31	Garnier's .....	60
Uele rubber .....	22	Gerard's .....	68
Ultramarine blue .....	182	Goodyear's, Charles ..	55
analyses of (tables)....	182	Hancock's, Charles ...	60
Green .....	184	Harris' .....	56
Uniting rubber to metals, Proc-		Havermann's .....	58
esses for .....	259	Helbronner and Bern-	
Adam's .....	260	stein's .....	61, 62
Daft's .....	261	Helm's .....	58, 65



Vulcanization—*Continued.*process of—*Continued.*

Henri's .....	61
Hot .....	55
Joselyn's .....	56
Marcy's .....	55, 56, 57
Meyer's .....	58
Mullee's .....	59
Murphy's .....	58
Newbrough and Fa-	
gan's .....	64
Newbrough's .....	57
Nickels' .....	60
Olivier's .....	61
Ostromislensky's .....	275
Parkes', Alex. ....	59
Parmelee's .....	57
Pressure cure .....	62
Raymond's .....	61
Rider's .....	58
Simpson's .....	57
Sulphur bath .....	63
Thomas' .....	56
Trotter's .....	55
Ultra-violet rays .....	61
Vapor .....	54, 59
Willman's .....	57
without sulphur .....	275
Accelerators for .....	282
Agents for .....	287
benzoyl peroxide .....	283, 284
mechanism of .....	280
nitro-compounds	
(table) .....	288
organic peroxides	
(table) .....	289
Patents for .....	285, 287
peroxides .....	282
trinitrobenzene .....	277, 278

## Vulcanized rubber analysis .... 312

Aniline method for min-  
eral fillers in .... 323Bureau of Standards'  
methods for .. 312, 314

## insulation, 30 per cent.

Para ..... 318 |

acetone extract .... 319

alcoholic potash ex-  
tract ..... 320 |

ash ..... 320 |

calculations ..... 320 |

chloroform extract.. 320

free sulphur ..... 319 |

general ..... 318 |

total sulphur ..... 320 |

unsaponifiable mat-  
ter ..... 319 |

waxy hydrocarbons 319

mechanical goods .... 315

Vulcanized rubber analysis—*Con.*

acetone extract ....	315
alcoholic-potash ex- tract .....	318
ash .....	317
barytes .....	317
calculations .....	318
free sulphur .....	316
specific gravity .....	318
sulphur of ash ....	317
total sulphur .....	316
outline plan .....	312
preparation of samples	314
grinding .....	314
hard rubber .....	315
soft rubber .....	314
reagents .....	315
acetone .....	315
alcoholic potash ...	315
barium chloride	
solution .....	315
fusion mixture ....	315
nitric acid-bromine..	315
remarks on .....	312
acetone extract ....	312
alcoholic-potash ex- tract .....	314
ash and sulphur in	
ash .....	313
barytes .....	313
chloroform extract..	314
free sulphur .....	313
rubber .....	313
specific gravity ....	314
total sulphur .....	313
Electrolytic methods for	332
Lead .....	332
Zinc .....	332
Joint Rubber Insulation	
Committee's meth- ods for .....	321
calculation .....	321
outline plan (table)...	322
Mt. Prospect Laboratory	
methods for .....	329
alcoholic-potash ex- tract .....	330
free sulphur .....	329
mineral fillers ....	329
rubber by weight.....	330
by volume .....	330
Rubber by wet combus- tion .....	324
Solvents for .....	328, 329
Sulphate sulphur method	328
Sulphide sulphur meth- od .....	326, 327
Vulcanizing ingredients .....	63
pressures (table) .....	70



- Vulcanizing ingredients—*Continued.*  
 processes ..... 54  
 temperatures (tables) .. 70  
 Vulcole ..... 70  
 Vulcoleine ..... 246
- WALNUT oil ..... 227  
 Wamba rubber ..... 23  
 Washers, Unvulcanized packing. 138  
 Washing rubber ..... 351  
 Waste rubber, Grades of.... 291, 293  
 Sources of ..... 293  
 Wax, Ant ..... 40  
 Bees ..... 156  
 Candelitta ..... 159  
 Carnauba ..... 159  
 Earth ..... 161  
 Japan ..... 217  
 Mineral ..... 167  
 Paraffin ..... 168, 223  
 Weber, Dr. C. O., analysis of  
 vulcanized rubber. 312  
 cellulose compound, ... 152  
 Wesson and Knorr, rubber by  
 wet combustion .. 324  
 West Indian rubber ..... 16  
 Wet heat cure ..... 54  
 Whalebone, Artificial ..... 141  
 Whaleite ..... 139  
 Wheat flour ..... 113  
 rubber ..... 139  
 Wheeler's reclaiming process... 298  
 White, Barium ..... 187  
 Beckton ..... 187  
*Blanc fixe* ..... 186  
 Bougival ..... 187  
 Calamine ..... 187  
 Charlton ..... 187  
 Chinese ..... 188  
 Constant white ..... 186  
 Fard's Spanish ..... 188  
 Fulton ..... 188  
 Griffith's ..... 188  
 Kremnitz ..... 188  
 lead ..... 113  
 Lithopone (lithophone). 188  
 Morat ..... 188  
 Moudan ..... 188  
 Oleum ..... 189  
 Orr's ..... 189  
 pigments for rubber... 186  
 Ponolith ..... 189  
 Ross's ..... 189  
 Rouen ..... 189  
 Rubber Makers' ..... 189  
 Spanish ..... 189  
 Troye's ..... 189
- White—*Continued.*  
 vitriol ..... 114  
 Zinc borate ..... 187  
 carbonate ..... 189  
 oxide ..... 189  
 sulphide ..... 191  
 Whiting ..... 113  
 Wichmann's substitute ..... 139  
 Wickham's machine ..... 51  
 Willman's rubber cure ..... 57  
 Winthrop gum ..... 139  
 Witherite ..... 114  
 Wolfert's substitute ..... 139  
 Wood ashes ..... 50  
 spirit ..... 246  
 Woodite ..... 139  
 Wormwood oil ..... 227  
 Wray's gutta-percha compound,  
 152, 387
- XANTHORRHOEA, *Arborea* ..... 153  
*Australis* ..... 153  
 gum ..... 175  
*Hastilis* ..... 153  
 Xelton ..... 152  
 Xingu rubber ..... 11  
 Xylene ..... 246  
 Xylodin ..... 175  
 Xylol ..... 246  
 Xylonite ..... 152, 175  
 "XX" brand zinc oxide ..... 190
- YALE blue ..... 183  
 Yellow, Antimony golden sul-  
 phide ..... 191  
 Arsenic ..... 192  
 Aureolin ..... 192  
 Barberry ..... 192  
 Cadmium ..... 192  
 Carsel ..... 102  
 Chrome ..... 193  
 Cobalt ..... 193  
 Dutch pink ..... 193  
 Gamboge ..... 193  
 gutta ..... 43  
 ocher ..... 193  
 pigments for rubber ... 191  
 Turner's ..... 102  
 Zinc ..... 193
- ZACKINGUMMI ..... 140  
*Zea mays* ..... 215  
 Zinc borate ..... 187  
 carbonate ..... 189

*Zinc—Continued.*

chloride .....	212
iodide .....	212
oxide .....	114, 189
“Green Seal” brand...	190
“Red Seal” brand....	190
“Special” brand .....	190
“White Seal” brand..	190
“XX” brand .....	190
sulphate .....	114

*Zinc—Continued.*

sulphide .....	69, 114, 191
white .....	191
yellow .....	193
Zingler’s Dermatine compound..	123
preservation of rubber	
goods .....	259
Zinsser’s barrel lining .....	140
Zuhl’s reclaiming process.....	299
Zylonite .....	175

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For Index see page 5

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# INDEX OF ADVERTISERS

Acushnet Process Co. ....	12
Aluminum Flake Co., The .....	28
Astlett, H. A. & Co. ....	7
Binney & Smith Co. ....	16
Birmingham Iron Foundry .....	36
Boston Yarn Co. ....	29
Buffalo Foundry & Machine Co. ....	33
Butcher, L. H. Co., Inc. ....	44
Cabot, Samuel, Inc. ....	Inside Front Cover
Canfield Oil Co., The .....	25
Carter Bell Manufacturing Co., The .....	25
Connecticut Mills Co. ....	30
Continental Rubber Co. of New York .....	12
Consulting Co., The .....	40
Cutler, David A. ....	38
Day, J. H. Co., The .....	36
Eagle-Pitcher Lead Co., The .....	18
Farrel Foundry & Machine Co. ....	34
Frazar & Co. ....	Opposite Back Cover
Henderson, F. R. & Co. ....	8
Hoggson & Pettis Manufacturing Co., The .....	35
India Rubber Publishing Co., The.....	10, 15, 17, 28, 37
Katzenbach & Bullock Co. ....	41
Loewenthal, R. M. & Co. ....	6
Manhasset Manufacturing Co. ....	32
Maywald, Frederick J., F. C. S. ....	40
Obalski, X. W., & Co. ....	9
Philadelphia Rubber Works Co. ....	13
Rare Metal Products Co. ....	27
Raven Mining Co. of Utah .....	19
Reichard-Coulston, Inc., ....	3
Roessler & Hasslacher Chemical Co., The .....	26
Scheel, William H. ....	28
Schrader's, A. Son, Inc. ....	42, 43
Scott, Henry L. & Co. ....	Inside Back Cover
Seaver & Co. ....	20
Somerset Rubber Reclaiming Works .....	14
Stamford Rubber Supply Co., The .....	21
Standard Emarex Co. ....	2
Stresen-Reuter & Hancock, Inc. ....	22
Tagliabue, C. J. Manufacturing Co. ....	32
Taylor, Armitage & Co., Inc. ....	31
Typeke & King, Ltd. ....	27
Tyson Brothers, Inc. ....	23
U. S. Rubber Reclaiming Co., Inc. ....	4
Waldo, E. M. & F. ....	Opposite Inside Front Cover
Weber, Lothar E., Dr. ....	39
West, H. T. Co., Inc. ....	24
Westmoreland Chemical and Color Co., The .....	26
Williams, C. K. & Co. ....	26
Wood, Charles E. ....	11

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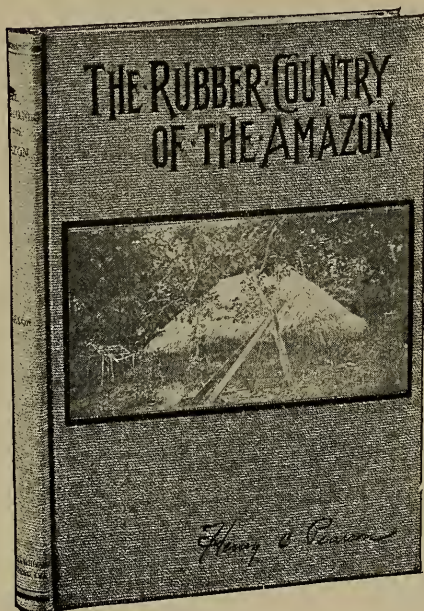
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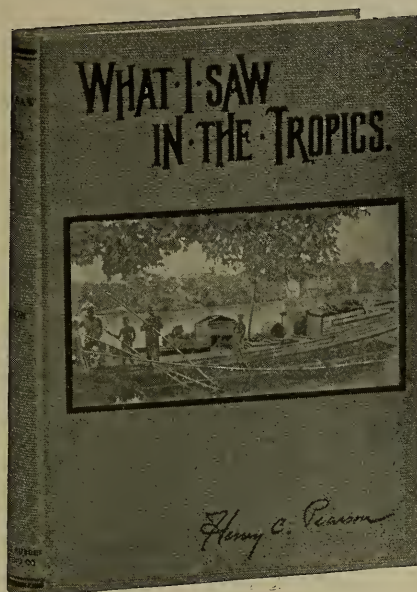
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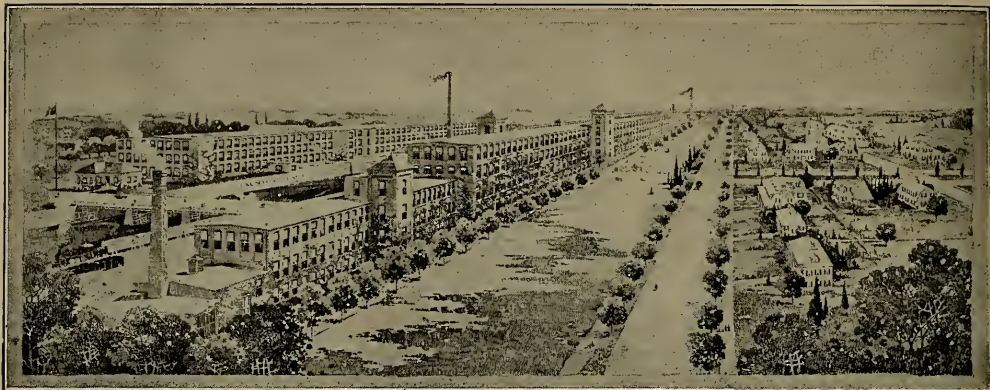
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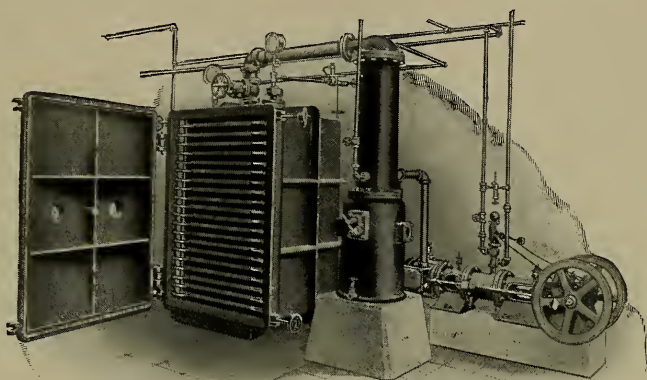
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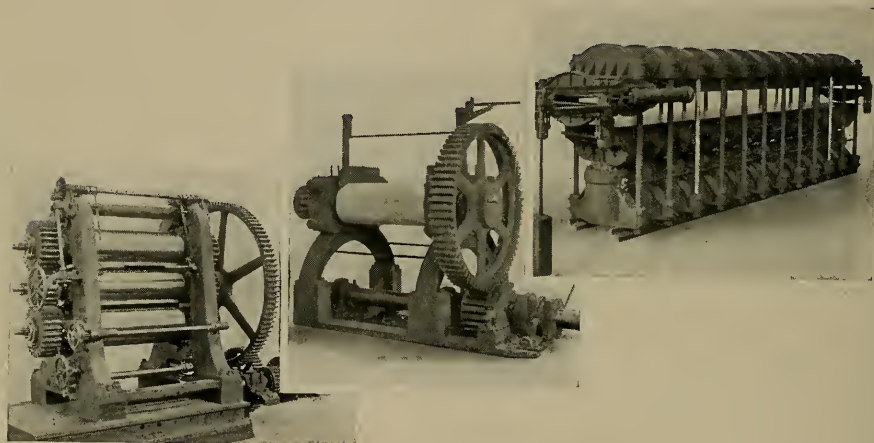
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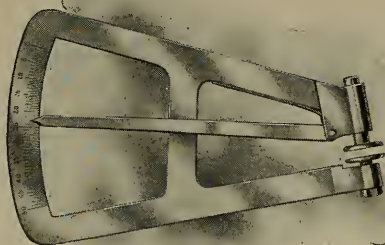
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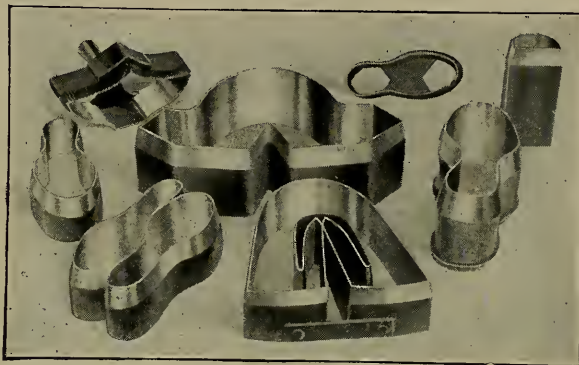
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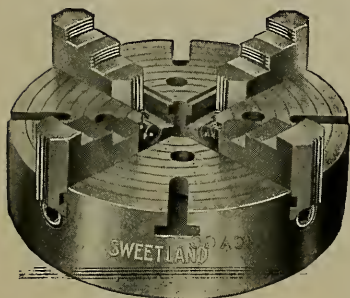


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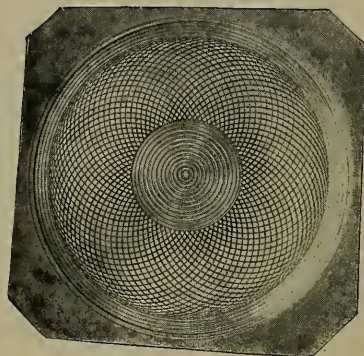
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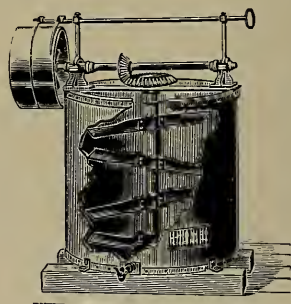
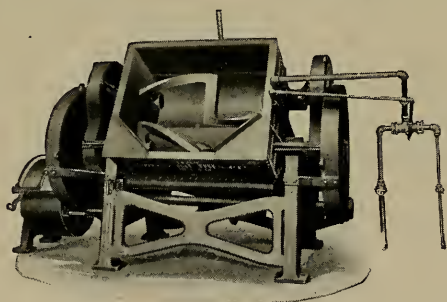
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Fig. 1  
One-half size



Fig. 2  
Two-third size

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Also occupy a preferential position in the favor of Motorists. Figure 1 shows the **GAUGE** with the standard base made to fit **TIRE VALVES** of the American type. As this style of **GAUGE** could not be used to measure the inflation of tires fitted with the European style Tire Valves, we have designed a **GAUGE** with the combination base (Fig. 2) which renders the **SCHRADER UNIVERSAL GAUGE** applicable to all **TIRE VALVES**. As illustrated in Figure 2, the **GAUGE** is ready for use on European type Valves. For use on the **SCHRADER UNIVERSAL VALVE**, simply unscrew the detachable foot or socket.

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Fig. 3  
One-half size

# Universal

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2198 Motor Tire Valve  
One-third Size

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Fig. 1  
One-half size



Fig. 3  
One-half size

The straight **VALVE PLUG** (Fig. 1) is intended for use with Wood's Valves on Bicycles and Motorcycles, and the bent **VALVE PLUG** (Fig. 2) for Wood's Valves on Aeroplane Tires. To attach, remove all of the upper parts of the Wood's Valve, except those as shown in Fig. 3. Replace with the **SCHRADER UNIVERSAL VALVE PLUG** selected, screwing it into the Wood's Valve Stem in just exactly the same way as the upper part of the Wood's Valve is attached, being careful to tighten the Nut sufficiently so that the Washer of the **PLUG** will make an air-tight joint in the Stem of the Wood's Valve. This arrangement not only obviates the necessity of constant repairing and the annoyance of Valve leakage due to the use of the ordinary Wood's Valve, but enables the user to employ a **TIRE PRES-SURE GAUGE** for ascertaining the pressure in his Tires, which is impossible when the Wood's Valve is used. The No. 2414 **COMBINATION VALVE CAP AND FOREIGN CYCLE PUMP CONNECTION** furnished with these **VALVE PLUGS** possesses two functions: First, that of a **VALVE CAP** as shown above; second, as a **PUMP CONNECTION** when the small threaded end B is screwed tightly into the **VALVE** so that an ordinary European Cycle Pump may be attached to the end A.

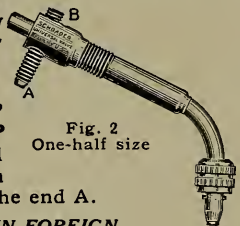


Fig. 2  
One-half size

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